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CHEMISTRY
FOR
TEXTILE STUDENTS

A MANUAL SUITABLE FOR TECHNICAL STUDENTS IN THE TEXTILE AND DYEING INDUSTRIES

BY

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PREFACE

THE present time, being one of reconstruction, is an opportune moment for the presentation of this work, as it is, we believe, the first attempt to put forward a fairly complete course on "Chemistry for Textile Students" suitable for the large and growing number of students who are taking up the technical study of textile industries from the truly scientific standpoint.

It is a noteworthy feature of the last "Census of Production," published in 1907, that, if we omit coal mining, whilst the cotton and woollen industries occupy respectively the first and fourth positions among the nine leading industries of the country as regards number of people employed, yet these industries employ a smaller percentage of well-trained technologists than any of the others. With one exception, the productivity, or net output in value per head of persons employed, is less in the case of textile industries, apart from chemistry and dyeing, than that of the other great industries of the country, and this is no doubt largely due to the small percentage of well-trained technologists employed.

Apart from the branches of bleaching and dyeing, it is only in very recent years that it has been realised, and only then by the most enlightened employers, that chemistry and physics play a most important part in the various operations used in the production of yarns and finished pieces. Recently, however, it has been recognised that Germany, in pre-war times, was getting far ahead of us, principally through the direct application of the sciences of chemistry, physics, and engineering to the processes of manufacture of textiles. Large manufacturers are now beginning to realise that specially trained textile-chemists and textile-engineers must be engaged for special research work, if progress is to be made which will enable us to keep pace with the competition of other great nations of the world. Germany was setting the pace in pre-war times, whilst our manufacturers were resting largely on the laurels of the past, with the result that certain branches of our great textile industry were fast passing to the continent; but in the near future other great nations of the world will have profited by the experience of Germany, and, if we are to maintain the traditions of the past, we must bring the sciences of chemistry and physics to bear to a greater degree on the study of textiles.

It is a necessary part of the training of the textile technologist, who will later be engaged in the production of yarns and finished articles, that he should have received a thorough grounding in the sciences of chemistry and physics. These subjects, as recognised by the Board of Education in pamphlets recently published, should form constituent parts of every technical systematic course of study for textile students. This is not often the case in evening courses at the present time, probably on account of the short time available in purely evening work, but with the introduction of day continuation schools more progress on sound scientific lines should be possible.

Although the scope of the work has been made fairly wide, so as to be generally useful to students in the textile and dyeing industries, the teacher of chemistry for textiles will have no difficulty in adapting the work to any special course suitable for students in cotton manufacture, woollen and worsted manufacture, dyeing, etc., and from the nature of the work he will know what parts may be omitted or dealt with more briefly.

The work makes no pretence of being an exhaustive study of the subject, but an attempt has been made to put forward a concise description of both inorganic and organic chemistry, on sound scientific lines, suitable for the student in textile industries; it should enable him to read larger and more specialised works intelligently and with profit.

A bibliography of works of reference is given, and these should be consulted for further information; it is only by the continuous use of standard works of reference, that the student will acquire facility in the use of them, and know where to find the necessary information when he is in difficulties. The authors have made use of some of these in the preparation of this book, and wish here to express their indebtedness to them.

My thanks are due to Mr Norman Bland, M.Sc., who has collaborated in the preparation of the greater portion of the material for Parts I, II and IV of the work, also to Miss Muriel North, and to Mr Harold D. B. North, for their assistance in the preparation of the manuscript, and to my daughter for her assistance in the preparation of drawings and photographs.

BARKER NORTH.

CITY OF BRADFORD TECHNICAL COLLEGE,
November, 1919.

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PART I

INTRODUCTORY

CHAPTER I

PHYSICAL STATES OF MATTER—PHYSICAL AND CHEMICAL CHANGES

MATTER: THREE STATES OF MATTER: PHYSICAL CHANGES: THE BALANCE AND METHODS OF WEIGHING: PHYSICAL AND CHEMICAL CHANGES: MECHANICAL MIXTURE AND CHEMICAL COMBINATION.

Matter.

The term matter is used to denote any substance which occupies space, and which possesses the property of weight. Although there are many different kinds of matter, and the forms are very diverse in appearance and in general properties, yet all these varieties may be classified as **solids**, **liquids** and **gases**.

In the case of **solids**, such as metals, minerals, vegetable matter, textile fabrics, etc., the colour, weight, lustre, and general outward appearance may be sufficient in many cases to distinguish one kind of matter from another, but in the majority of cases, experiments will be necessary in order to distinguish the different forms of matter or determine their composition.

Experiment 1. Required: Test tubes, bunsen burner, iodine, natural graphite (flaky).

Place a small piece of graphite (carbon) in a dry test tube and heat the solid gently in the bunsen flame; then repeat the experiment, using a small quantity of iodine, but in each case not more than one or two flakes or crystals need be taken. Make careful observations, and enter in notebook as follows:

Substance used	Experiment made	Observations	
		Before heating	After heating
1. Graphite (carbon)	Heated in tube	Black shining flaky crystals	No change
2. Iodine	do.	do.	Gives violet vapour when hot, and black crystals on cool part of tube

Note: The student must learn to make records similar to the above, but adapted to the form of experiment which is being carried out; in some cases, too, it may be advisable to add an additional column, headed "Inference." In carrying out any of the experiments detailed in the following pages, the student should, from the commencement, accustom himself to making exact observations and accurate records of what has taken place, whether these agree with what appears in the text or not. In some cases a slight modification in the method of working may entirely alter the observations which are made.

In the case of **liquids**, such as water, oil, alcohol, ether, etc., these may be mobile or viscid, colourless or coloured, inflammable or non-inflammable, but experiments are generally necessary in order to distinguish one liquid from another.

Experiment 2. Required: Sand bath, alcohol, ether.

Pour a few drops of alcohol into the sand bath and light the liquid, then repeat the experiment with a little ether.

Special care must be taken at all times in working with ether to avoid the neighbourhood of flames when pouring the liquid, and to be careful not to pour from a bottle over a bench sloping towards a distant flame (see p. 255).

The sand bath should therefore be allowed to cool before pouring in the ether. Notice that the flame is much less luminous in the case of alcohol than with ether, although the alcohol flame becomes much more luminous as the temperature rises; also notice that the ether is more volatile than the alcohol, so that with approximately equal bulks of the two liquids, the alcohol flame lasts longer.

Gases, such as coal gas, air, oxygen, hydrogen, chlorine, etc., may be coloured or colourless, lighter or heavier than air, inflammable or non-inflammable, etc., but with gases it is almost always necessary to make experiments in order to distinguish one kind of matter from another.

Experiment 3. Required: Gas jars, rubber tubing connected to a coal gas supply.

Connect the piece of rubber tubing to a gas supply, and pass the open end of the tube to the top of a gas cylinder held mouth downwards. In this way

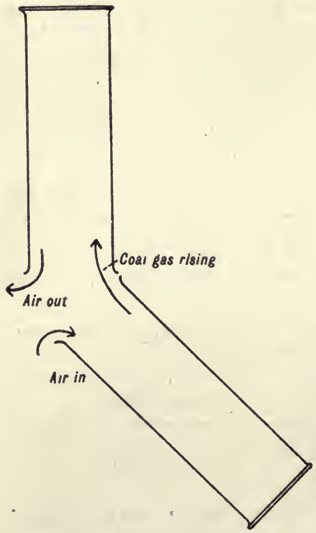

Fig. 1. Pouring coal gas upwards from one jar to another.

the gas jar may be filled with coal gas by displacing the air. The method of collecting the gas shows that the coal gas is lighter than air, and this may be further demonstrated by pouring the gas upwards into a second inverted cylinder as shown in Fig. 1. The escape of the gas from one cylinder to another may be shown by applying a lighted taper to each cylinder, when the gas will either burn or explode slightly.

Three states of matter. Physical changes.

The three forms in which matter can exist, namely, solid, liquid, and gas, are termed the three physical states of matter, and most bodies under suitable conditions of temperature and pressure can exist in each of the three physical states. For example, ice, if it is heated, passes into the liquid form, known as water, and if the water is still further heated, it passes at its boiling point into the gaseous form known as steam.

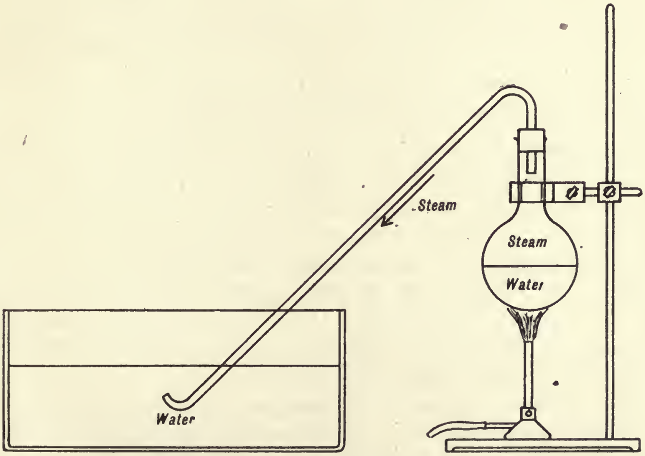

Fig. 2. Invisibility of steam and change from one physical state to another.

Experiment 4. Required: 250 c.c. flask, retort stand and clamp, wood cork to fit flask, cork borers, glass tubing, $\frac{1}{4}$ in. in diam., pneumatic trough containing water.

Fit up the apparatus shown in the sketch (Fig. 2). A cork should first be chosen which is slightly large for the neck of the flask, so that, after rolling under the sole of the foot to soften it, the cork will fit tightly into the flask. The glass tube is bent at an acute angle by heating in a **fish-tail** flame, the glass being continually rotated during the heating until soft and pliable, when it may be bent to the angle required. The sharp edges of the glass should be removed by slightly fusing the ends in an ordinary bunsen flame. To fit the glass tube, the cork must be bored and for this purpose a cork borer must be chosen, which is as nearly as possible equal to, but not larger than, the glass tube in diameter.

The flask is half filled with water, and heated with a bunsen flame, care being taken that the flame does not directly heat the glass above the level of the water. The trough may at first be removed, and when the water is boiling the following observations may be made:

(1) That the gas above the water is invisible, thus proving the invisibility of steam.

(2) That part of the steam condenses in the long sloping tube, reforming water.

(3) That a cloud forms at the mouth of the tube, though careful observation shows that close to the end of the tube itself the gas is quite invisible; the cloud consists of minute particles of liquid water.

If the trough is now placed in the position shown, the steam issuing from the mouth of the tube will be rapidly condensed by the cold water in the trough, and a slight rattling noise will be heard. If the flame is withdrawn, the water first creeps up the sloping tube until a little of the cold water enters the flask, when there is a sudden inrush, the flask filling up with water, thus proving that all the air was expelled from the flask, and that the gas above the water consisted only of steam.

Experiment 5. Required: Boiling tube, bunsen burner, roll sulphur.

Heat a small quantity of roll sulphur in a boiling tube, very gently at first, until the sulphur is entirely melted, forming a pale amber-coloured mobile liquid. Then increase the temperature, when the liquid will become very dark and viscid, and finally boil forming a dark red vapour. In the cool part of the tube some of the sulphur will condense, forming a yellow solid and a yellowish-red liquid. On cooling, the sulphur vapour first disappears, and the thick dark liquid then becomes lighter in colour, finally passing into the yellow solid.

These changes, from solid to liquid or liquid to gas, or the reverse changes, are known as physical changes, the change in properties being only temporary, so that when the disturbing influence is removed, the substance passes back to its original condition.

Many other examples may be given of physical changes, *e.g.*, a piece of platinum wire on heating glows white hot, but on cooling returns to its original condition, without change in weight or permanent change of other properties having occurred.

A piece of sealing wax when rubbed with flannel becomes electrified, so that it will attract light particles, such as small pieces of paper, pith, etc., but on standing for a short time it loses this property. If an electric current is passed through a wire wrapped round a piece of *soft iron*, the latter acquires temporarily the property of attracting iron and steel. When the current ceases, the iron loses its magnetism. All these are examples of physical changes.

The balance and methods of weighing.

In many of the succeeding experiments it will be necessary to weigh out exact quantities of substances, and a short description of the chemical balance and the weights used, Fig. 3, will therefore be given, as it is of the greatest importance that the student should from an early stage be able to use a chemical balance with discretion and care.

Chemical balances are made of varying degrees of accuracy, and one which responds to a difference in weight of 1 centigram (·01 gram) when loaded with a weight of 50 or 100 grams will be suitable for the experiments in Part I. It should be noted that the balance is not so sensitive when loaded with the heavier weights, and also that there is a definite load for each balance above which there is a danger of straining the parts of the balance, particularly the beam. This load is the total weight put upon any one pan of the balance. In many preparations, what is termed a "rough" balance may be used, which is sensitive to about 0·1 grm. when loaded.

For more accurate analytical work, balances are made to respond to $\frac{1}{10}$ of a milligram when full loaded, such as is shown in Fig. 3, the balance being contained in a glass case which should be closed when the final adjustment to a fraction of a centigram is being obtained. The rougher and less delicate balance, such as is employed for the experiments in the early part of this work, should however be used just as carefully as a more sensitive one; no solid or liquid must be allowed to come into contact with the pans of the balance, the substance being weighed in a bottle, beaker, basin or on a watch glass.

The balance consists essentially of a beam supported by means of a steel or agate knife-edge on an agate plane, and carrying two pans similarly supported at the ends at equal distances from the central support. The beam and pans, when the balance is not in use, are supported, so as to remove the knife-edges from the planes, and substances and weights should never be placed on the pans when the beam is free to swing. This is of great importance, otherwise the balance will soon lose its sensitiveness. The movement of the beam is observed by a pointer swinging over a scale, and the two sides are balanced, and the correct weight obtained, when the pointer swings equally on each side of the central line of the scale. In more accurate analytical work, when using a "rider," which is moved on the beam for obtaining the fractions of a centigram, it is advisable to weigh by a system of vibrations for determining the point of rest of the index hand, but for the experiments described in Part I it is sufficiently accurate to add or withdraw weights until the pointer vibrates equally on each side of the central line of the scale.

The weights must be accurate and should range from 50 grams to

1 centigram. They are placed on the right-hand pan of the balance and the substance to be weighed on the left. The student must guard against guessing the weight of the substance, or trying the weights indiscriminately, as this generally results in a loss of time; the weights should always be

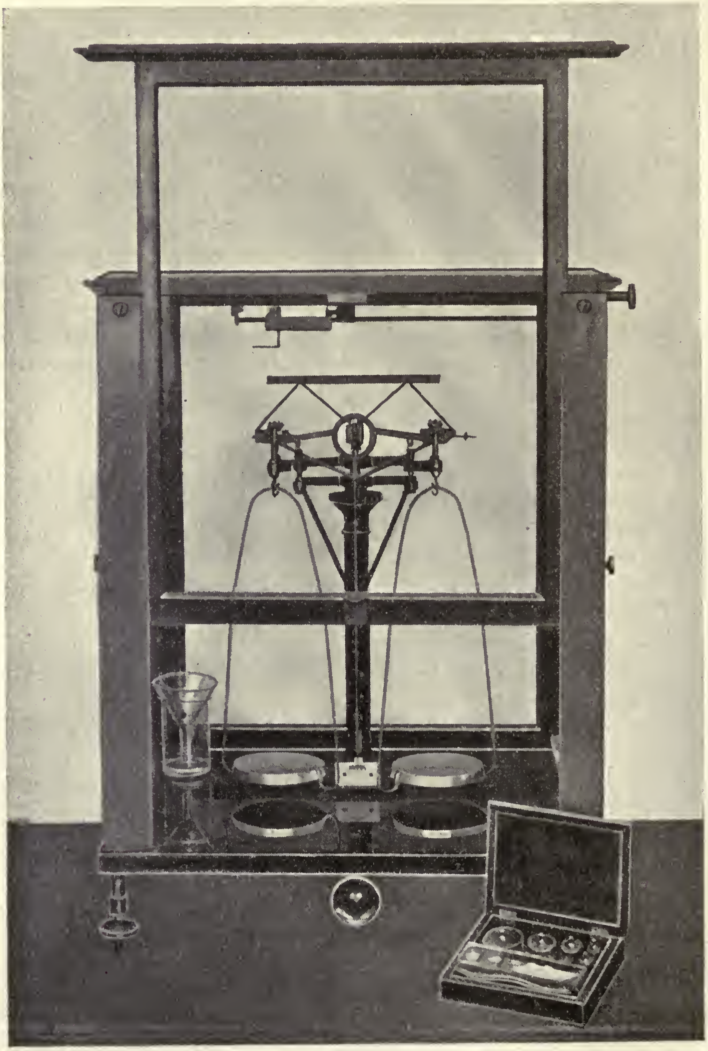

Fig. 3. The chemical balance and weights.

put on the pan in sequence, after estimating in the first place only whether the weight of the substance is over 50 grams, between 20 and 50, 10 and 20, etc. If the 20 gram weight has been tried and found too heavy, it is replaced in the box and the 10 gram put on the pan; if this is too light, the 5 gram weight is added, then the 2 gram, and so on till the centigram weight has been used, care being taken that none of the weights are touched with the fingers. Thus, if the following weights are on the pan when balanced: 10 grm., 5 grm., 1 grm., ·2 grm., ·1 grm., ·05 grm., ·02 grm., the total weight will be 16·37 grms. The total weight should always be checked from the weights on the pan, and the empty spaces in the box, *then immediately entered up in the notebook*, with a clear statement as to what the weight refers to; the total weight should finally be checked as the individual weights are returned to the box.

Distinction between physical and chemical changes.

Experiment 6. Required: Bunsen burner, platinum wire, magnesium ribbon, dilute hydrochloric acid, test tubes, balance and weights, porcelain crucible and lid.

Heat the platinum wire in the bunsen flame; the wire becomes almost white hot but on cooling returns to its original condition. If the wire is weighed before and after the experiment, there is no change in weight, so that on heating it undergoes only a temporary change in properties, or, in other words, the change is a physical one.

If the magnesium ribbon is heated in the flame, it takes fire and burns with a very brilliant flame, forming a white solid and some white fumes, the latter consisting of finely divided particles of the solid. The main portion of the white solid retains the shape of the ribbon, but if pressed in the fingers it falls to powder. That some permanent change has taken place may be shown by the addition of a little dilute hydrochloric acid to a piece of the metal and to a little of the white powder; in the case of the metal it dissolves with the liberation of gas, but the white solid dissolves in the acid without effervescence. Further, if a definite weight of the metal is burnt in a porcelain crucible with lid so as to prevent loss of white fumes, it may be shown that the white solid is heavier than the metal from which it is produced. It may also be proved that there is a definite relationship between the weights of metal burnt and of white solid formed. Such a change, in which there is a permanent alteration in weight and in the properties of the substance, is known as a chemical change.

Distinction between mechanical mixture and chemical combination.

It is often of importance to distinguish between actions which result merely in the production of a mechanical mixture, and those which result in the chemical combination of the constituents. The main differences will be found to be in the relationship between the properties of the substance and the individual properties of its constituents, and the relative proportions of the constituents. In the case of a mixture, in which the constituents are merely blended, the properties of the mixture will be regulated by the individual substances present, as each body will retain its own characteristic properties; whereas, in the case of chemical combination, the substances uniting together lose their individual properties, and the new body formed acquires entirely distinct properties.

Further, heat is generally evolved during chemical combination, and it can also be shown that substances combine together chemically in certain definite proportions by weight, which will depend on the nature of the bodies reacting together; in the case of substances which are mixed together, without chemical action taking place, the blending may be carried out in any proportion. Some of these differences may be shown by the following experiments.

Experiment 7. Required: Bunsen burner, test tubes, iron filings, flowers of sulphur, magnet, pestle and mortar, carbon disulphide, watch glass.

Grind together in the mortar iron filings and sulphur, the latter being about twice the bulk of the iron. A yellowish or greenish powder will be the result, but that this is a mixture may be shown in several ways. A magnet, if passed over the mixture, will attract the iron, and, although some of the sulphur and iron may still stick together, by repeating the process several times an almost perfect separation may be obtained. Examination with a microscope will show the particles of iron and sulphur lying side by side in the mixture.

Sulphur is soluble in carbon disulphide, and if a little of the mixture is put into a test tube and well covered with this liquid, the sulphur will disappear on warming leaving the iron.

This liquid must be heated with great care as the carbon disulphide is very volatile, and the vapour is inflammable.

If the iron is allowed to settle in the liquid, a portion of the clear carbon disulphide solution may be decanted on to a watch glass, and by allowing the carbon disulphide to evaporate, some of the original solid sulphur may be recovered.

If some of the original mixture, preferably made by mixing 14 grams of iron with 8 grams of sulphur, is put into a test tube, and heat applied to the upper portion of the mixture, a chemical action may be started. The portion heated suddenly rises in temperature and glows red hot, and without the further application of heat, the chemical action, accompanied by the production of heat, passes throughout the mass.

The resulting mass when cool has a greyish-black colour, and if powdered gives a dull black powder. If the powder is tested with a magnet, a very slight quantity of free iron can generally be extracted, but the amount is very different from that obtained from the mixture, and the extraction of this small quantity does not alter the colour of the remainder. Carbon disulphide will not extract sulphur from the black powder, the latter having properties very different from the original iron and the sulphur.

Experiment 8. Required: Test tubes, large watch glass, beaker about 4" high, glass rod, sugar, strong sulphuric acid, alcohol.

Mix in a test tube about equal quantities of alcohol and water. No chemical action results, and the water and alcohol retain in the mixture their individual properties. Pour the liquid mixture into the watch glass and apply a light; the alcohol may be almost entirely burned away, leaving almost pure water. Measure the liquid remaining, and show that it is approximately equal in bulk to the original volume of the water.

Make a strong syrupy solution by dissolving two or three lumps of ordinary sugar in a small quantity of water in the beaker, employing a gentle heat if necessary. When the liquid is quite cool, pour slowly about an equal bulk of concentrated or strong sulphuric acid into the syrup, and stir with a glass rod during the addition. The liquid will froth up into a porous mass of carbon, which is liberated from the sugar by the chemical action of the sulphuric acid upon it.

> **Important note:** Great care should always be taken in pouring concentrated sulphuric acid into water, as much heat is generated, and unless the acid is poured in slowly in a thin stream and with constant stirring, the liquid may spurt violently, projecting acid out of the vessel. *Never pour water into concentrated sulphuric acid*, and on no account should concentrated acid be added to a strong alkaline solution.

Experiment 9. Required: Schweppe's soda water bottle with pointed end, supply of oxygen, petrol.

This experiment may be delayed until oxygen has been dealt with (see p. 27), if a supply of oxygen is not available. Fill the soda water bottle with oxygen gas, and pour a few drops of liquid petrol into the bottle; cork tightly and shake well. The petrol will give off gas, which will form with the oxygen a mixture of gases similar to the explosive mixture employed in a motor car, except that pure oxygen is employed instead of air. The bottle should be well wrapped up in two or three dusters or towels, the cork withdrawn and the gases lit at a flame. A very violent explosion will ensue, due to the chemical action between the gases producing an intense amount of heat which causes the gases to suddenly expand, thus setting the air in rapid vibration and producing the noise of the explosion.

Until the flame is applied, the bottle contains a mixture of gases only, but on the application of a light a chemical action is started between the petrol vapour and the oxygen gas.

CHAPTER II

PRELIMINARY STUDY OF THE ATMOSPHERE

WEIGHT OF THE ATMOSPHERE: PRESSURE OF THE ATMOSPHERE: THE BAROMETER: BOYLE'S LAW: CHARLES' LAW: VAPOUR PRESSURE.

Weight of the atmosphere.

The atmosphere is a mixture of gases surrounding the earth, and forming an envelope which extends many miles from its surface. As already stated, a gas is a form of matter, and may be shown to possess weight; this may be demonstrated in the case of the atmosphere by the following experiment.

Experiment 10. Required: 1000 c.c. round bottom flask, 1-hole I.R. cork, short pieces of glass and rubber tubing and pinch cock.

The piece of glass tubing, with rubber tubing attached, is passed through the hole in the cork, which is then fitted tightly into the flask containing about 100 c.c. of water and this is boiled for several minutes. The air in the flask is gradually replaced by steam, and when the steam issues freely from the flask, the pinch cock is placed on the rubber tubing, whilst the heating is simultaneously stopped. The flask is allowed to cool, and is carefully weighed.

During the cooling, the greater portion of the steam is condensed, and, if the pinch cock has held tight, no air will have entered and a partial vacuum will have been formed. On opening the pinch cock, therefore, air will enter so that on again weighing the flask, the weight will be found to be greater by an amount equivalent to the weight of air entering the flask. By finding the volume of the flask and the volume of water remaining after boiling, the volume of the air, the weight of which has been determined, may be found. From these figures, the weight of 1 litre of air at the temperature and pressure of the air in the room may be approximately determined.

Pressure of the atmosphere.

As the atmosphere possesses weight, it must therefore exert pressure, and this may be demonstrated by the following series of experiments.

Experiment 11. Required: A gas jar, a stiff card such as a post card, glass plate.

The jar is filled completely with water, covered with the post card so as to exclude any bubbles of air, and then inverted, the card being meanwhile held in position. The support to the card may then be removed, and the card is held against the mouth of the jar and the column of water supported by the pressure of the atmosphere. Instead of a card, the glass plate may be used, the experiment being performed in a similar manner. If air is introduced into the jar, the card or plate will be forced away by the weight of water, as the air now exerts a pressure inside the jar equal to the pressure of the atmosphere outside.

Experiment 12. Required: A can made of thin "tin," rubber stopper, tripod and bunsen burner.

A small quantity of water is placed in the can, and the water boiled to displace the whole of the air. The can is tightly corked, and allowed to cool. As the steam condenses, the pressure of the air on the outside will cause the can to collapse. Instead of cooling the can by exposure to air, it may be plunged into a deep vessel of water, when it will rapidly collapse, the pressure of the air in this case acting on the surface of the water and through the water on the surface of the tin can.

Experiment 13. Required: Glass lamp chimney or wide glass tube about 2″ diam. and 12″ long, piece of sheet rubber (a scrap piece from the rubber sheet used for the bellows of a foot blowpipe is suitable), 1-hole rubber cork to fit tube, short piece of glass tubing, copper wire, I.R. pressure tubing and water pump.

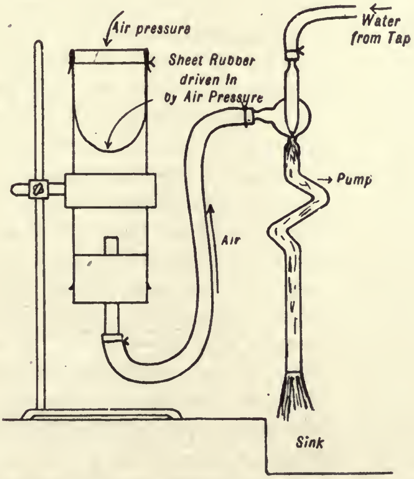

Fig. 4. Pressure exerted by the atmosphere.

The piece of sheet rubber is tightly wired on to one end of the wide glass tube, which is fitted at the opposite end with the rubber cork and glass tube, as in Fig. 4. The narrow glass tube is connected by pressure tubing to the water pump, which is connected again to a water supply at a good pressure. By means of the pump, the glass tube is exhausted, and the pressure of the outside air drives the sheet rubber inwards in the form of a balloon, Fig. 4, until the rubber is ultimately burst by the air pressure with a loud report.

The barometer.

The pressure of the air is sufficient to support a column of water about 30′ high, such a column, with a cross-section of one square inch, weighing about 15 lbs. A column of mercury 1 sq. in. in cross-section, measuring about 30″ long, weighs also 15 lbs., and this column, therefore, may also be supported by the atmospheric pressure. The pressure of the air is usually expressed in terms of such a mercury column, termed a barometer, which may be illustrated by the following experiment.

Experiment 14. Required: $\frac{1}{4}''$ glass tube, 30″ long, sealed at one end, mercury and mercury trough.

The glass tube is *nearly* filled with mercury, the open end closed with the thumb, and the tube inverted to pass the bubble of enclosed air up and down the tube, thus removing the small bubbles of air adhering to the inner surface of the glass. The tube is now completely filled with mercury, the open end again closed with the thumb and placed upright in the dish of mercury, with the open end below the surface, as in Fig. 5. On removing the thumb, the mercury falls in the tube until the level of mercury in the tube is approximately 30″ vertically above the level in the trough. This column of mercury is supported by the pressure of the atmosphere, and as this varies from day to day, the height of the column will vary correspondingly, becoming shorter when the pressure is less and *vice versa.* The weight of the column of mercury is actually equal to the weight of a column of the atmosphere of the same cross-sectional area. If the tube is inclined, the mercury will approach the closed end and may strike it with a sharp metallic click, as the space above the mercury is an almost perfect vacuum. It should be noted, when the tube is inclined, that the level of mercury in the tube remains 30″ vertically above the level in the trough, until the mercury reaches the closed end of the tube. The apparatus, as thus arranged, forms a simple *barometer.*

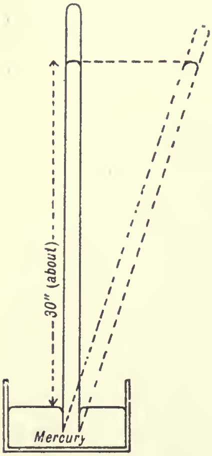

Fig. 5. Simple barometer.

Note: The mercury for this experiment must be thoroughly cleaned and dried. Unless the mercury is amalgamated with other metals, such as zinc or copper, it may be purified by heating in a large porcelain dish on a tripod standing in a wood mercury tray until the mercury begins to fume; the mercury is then filtered, using a filter paper in a glass funnel with a small pinhole in the apex of the paper.

The glass tube must also be carefully cleaned and dried. The tube is first thoroughly cleaned, if necessary by rinsing with a little nitric acid, then washed with water, and finally rinsed first with alcohol and then with a little ether. By blowing air from the foot-bellows for a few minutes to the bottom of and through the tube, the trace of ether is vaporised and the tube is left thoroughly dry.

Small bottles of ether and alcohol may be kept for drying glass tubes, flasks, or other vessels in this way, but care must be taken to remove every trace of vapour, if necessary, by carefully and gently warming the tube or vessel. It must be remembered that a mixture of ether vapour with air or oxygen may be explosive, and due care must be taken not to bring a flame near to such a mixture.

The following experiment shows that the barometric column is supported by the pressure of the air on the mercury in the trough.

Experiment 15. Required: Barometer tube as in last experiment, 8 oz. wide-mouth bottle, 2-hole I.R. cork to fit, tap tube, mercury, I.R. pressure tubing and pump, $\frac{1}{2}''$ or $1''$ specimen tube about $1''$ long.

The barometer tube is fitted through one hole in the cork, and the tap tube is bent at right angles and inserted in the second hole. The barometer tube is filled with mercury and placed in a trough of mercury as in last experiment, the specimen tube, supported by a piece of copper wire tightly wrapped round it, being now put underneath the open mouth of the tube and used as a small mercury trough to transfer the open end of the barometer tube to the 8 oz. bottle half filled with mercury, as in Fig. 6. The cork may now be adjusted, so as to fit the bottle tightly, and the tap tube is connected to the water pump. When the air is exhausted, the mercury falls in the tube according to the degree of exhaustion, and, with a good pump, the level may be drawn down nearly to the level in the bottle. On again admitting air to the bottle, the mercury is driven up to its original height.

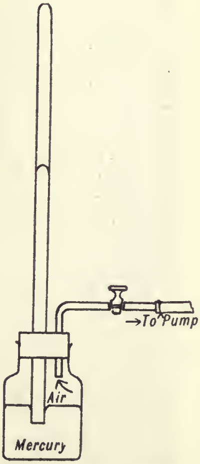

Fig. 6. The barometric column, supported by the pressure of air on the mercury in the trough.

Relationship between pressure and temperature of a gas and its volume. In determining the mass of a gas, it is often more convenient to measure its volume than to weigh it, but as the volume of a given mass of gas varies with change of pressure and temperature, it is necessary to know the relationship which exists between changes of pressure and temperature and changes of volume.

Boyle's law—pressure and volume.

By increasing the pressure upon a given mass of gas, the volume is reduced and *vice versa.* This is expressed in the law of Boyle thus: "The volume of a gas, if the temperature remains constant, is inversely proportional to the pressure," whence "the temperature remaining constant, the product of the pressure and the volume is a constant number."

Experiment 16. Required: Glass tube about 50″ long, mercury, retort stand and clamp, metre scale.

The tube is carefully cleaned and dried, and bent into a U-shaped form, with a long limb and a short one, the latter end being then sealed in the blowpipe flame. Mercury is poured into the tube, which is tilted to allow bubbles of air to pass round the bend, until the level of the mercury is at the same height in each limb, and the tube is then supported vertically in the stand and clamp as in Fig. 7.

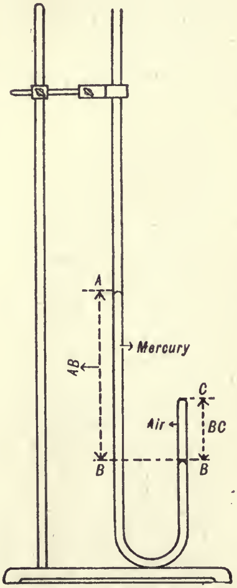

Fig. 7. Boyle's law tube.

The length of the column of the air is measured in millimetres, and the number obtained may be used to represent the volume (V), at the pressure (P), *viz.*, at the atmospheric pressure as shown by the barometric column measured in millimetres. Mercury is again poured into the open limb, to the level at A, and the mercury rises in the closed limb to the level, say B. The new volume (V') is represented by the length BC in millimetres; the new pressure (P') on the gas will be the pressure of the atmosphere in millimetres plus the pressure represented by the vertical column of mercury AB in millimetres.

It will be found that:

$$P \times V = P' \times V'.$$

Several readings should be taken in this manner to verify the above result. From this it follows that the volume is inversely proportional to the pressure.

Example illustrating the use of the law: 100 c.c. of air are measured at 745 mm. pressure, what will be the volume at 760 mm.?

Here the old volume (V) = 100 c.c.; the old pressure (P) = 745 mm.

The new pressure (P') = 760 mm., and it is required to find the new volume (V') at the new pressure.

$$P \times V = P' \times V',$$

$$\therefore \quad 745 \times 100 = 760 \times V',$$

$$V' = \frac{745 \times 100}{760}.$$

A form of apparatus which may be conveniently used for demonstrating the law is shown in Fig. 8. The level of the mercury in the open limb is easily adjusted by means of the sliding mercury reservoir (*A*), and the level is read off on the metre scale. The volume of the gas in the short stoppered graduated tube is read in cubic centimetres, and the level of the mercury in this tube noted on the metre scale; the pressures are thus easily deduced, when the height of the barometer is known. The gas in the graduated tube is dried by passing through the drying tube before use.

It may also be noted that the law holds good for pressures below atmospheric. If the level of mercury in the reservoir, *A*, is below the level in the stoppered tube, the difference between these levels subtracted from the barometric pressure will give the pressure that the gas is under.

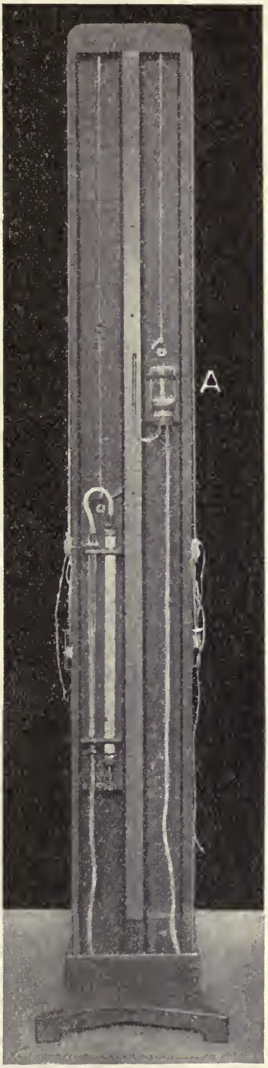

Fig. 8. Boyle's law apparatus.

Charles' law—temperature and volume.

When the temperature of a given mass of gas is increased, the pressure remaining constant, the volume increases, and *vice versa*. This expansion and contraction is found to be $\frac{1}{273}$ of the volume of the gas at 0° C., for each 1° C. change of temperature, and this is known as Charles' law. It therefore follows that 1 litre of a gas, say air, at 0° C. becomes $1\frac{1}{273}$ litres at 1° C., $1\frac{2}{273}$ litres at 2° C., or retaining still the same proportion:

273 litres at 0° C. become 274 litres at 1° C.
" " 275 " 2° C.
" " 276 " 3° C.
" " $273+t$ " t° C.

From this rate of expansion, it also follows that the above volume (273 volumes at 0° C.) will become 272 volumes at −1° C., 271 at −2° C., and zero at −273° C. The volume of all gases should thus become zero at this temperature (−273° C.) which has been named the absolute zero of temperature; as a matter of fact, all known gases are liquefied before this temperature is reached.

On the **Absolute scale of temperatures,**

−273° C. = zero or 0° *A*.
−272° C. = 1° *A*.
0° C. = 273° *A*.
1° C. = 274° *A*.
2° C. = 275° *A*.
t° C. = 273 + *t*° *A*.

Charles' law may, therefore, be stated thus: "The volume of a gas, when the pressure remains constant, is proportional to its absolute temperature."

The law may be demonstrated by the use of the apparatus shown in the sketch (Fig. 9). *A* is a measuring tube graduated in c.c., and connected to an adjustable pressure bulb, *B*, by I.R. pressure tubing, the tubes and bulb containing mercury and enclosing a convenient volume of air in the tube, *A*. *C* is a surrounding jacket through which steam may be passed, or, by disconnecting at the top of the jacket and plugging the outlet tube at the bottom, crushed ice and water at 0°C. may be poured in to cool the air to the freezing point of water. The volume of air in c.c. is read off, both at the temperature of steam and melting ice, the pressure being brought in each case to atmospheric pressure by adjusting the height of the bulb *B*, so that the levels of mercury in *A* and *B* are at the same height.

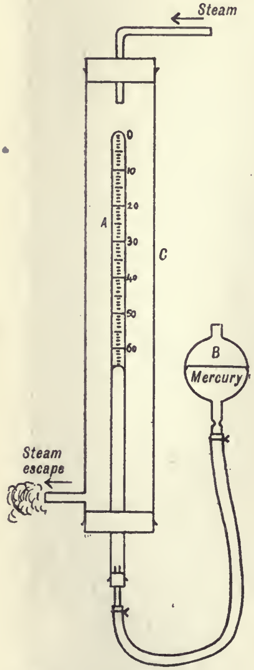

Fig. 9. Charles' law apparatus.

Let x c.c. = vol. of air at 0° C.
and y c.c. = " 100° C.

then x c.c. for a rise of 100° C. starting from 0° C. expand $y-x$ c.c.

1 c.c. for a rise of 100° C. starting from 0° C. expands $\frac{y-x}{x}$

1 c.c. " 1° C. " " $\frac{y-x}{x \times 100}$

$= \frac{1}{273}$ about.

Example illustrating the use of the law: 100 c.c. of air are measured at 15° C. What will be the volume at 0° C.?

From Charles' law it is known that

$$288 \text{ volumes at } 15^\circ \text{ C. become } 273 \text{ volumes at } 0^\circ \text{ C.}$$

$$1 \quad \text{"} \quad \text{becomes } \frac{273}{288} \quad \text{"}$$

$$100 \text{ c.c. at } 15^\circ \text{ become } \frac{273 \times 100}{288} \text{ c.c. at } 0^\circ \text{ C.}$$

Water vapour in the atmosphere—vapour pressure.

The atmosphere always contains a certain amount of water in the form of water vapour, and the amount varies from day to day, being dependent principally upon the temperature. The amount present in the air, or in any other gas, is usually expressed by the pressure which it exerts as represented in millimetres of mercury, and this may be illustrated in the following experiment.

Experiment 17. Required: Three dry barometer tubes, trough of mercury, retort stands and clamps, pipette with point bent into hook-like form, ether.

The three tubes are each filled with mercury, inverted into the mercury trough to form simple barometers, and supported by the stands and clamps in the positions shown in Fig. 10. A little water is drawn up into the pipette, which is then hooked under the mouth of one of the tubes and a small quantity of water is carefully blown into the mercury. The water rises to the top of the barometer column and rapidly vaporises in the vacuum, depressing the mercury for a short distance, and a portion of the water remains permanently on the surface of the mercury. The space in the tube is now saturated with water vapour, and the addition of more water merely adds to the amount of liquid in the tube. Under these conditions, the water vapour in the space above the mercury is exerting its maximum pressure at the temperature of the room, and, at 15° C., this is equal to 12·7 mm. of mercury, that is, the mercury column is depressed by this amount. This is termed the maximum tension of water vapour at this temperature, and its

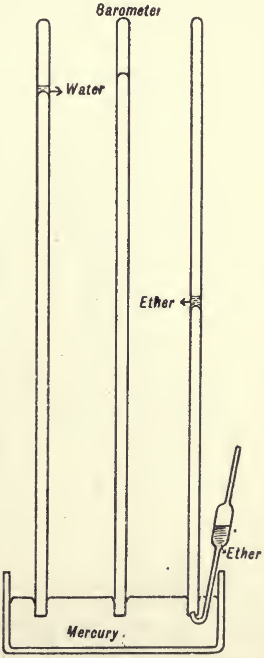

Fig. 10. Showing the vapour pressures of water and ether at atmospheric temperatures.

value is independent of the nature of the gas, the pressure of the gas or the form of the vessel, being merely dependent upon the nature of the saturating vapour and the temperature of the space occupied by the gas.

If a little ether is passed into a second barometer tube, the mercury will be very suddenly depressed, and, when the ether is permanent upon the surface of the mercury, the level of the latter will have been depressed about 400 mm. This great pressure of ether vapour at ordinary temperatures emphasises the point already mentioned with regard to the use of ether, and the danger in pouring from a bottle. The space above the liquid will always be saturated with ether vapour, and about half the pressure of the gas will be due to ether vapour, so that the composition of the gas may be assumed to be approximately 50 per cent. air and 50 per cent. ether.

It follows, also, that whenever a gas is collected over water, the usual method of collecting gases, the gas will be saturated with water vapour, as the vapour exerts its maximum pressure in a closed space at any temperature, when it is in contact with its own liquid. In such a case the pressure of the gas is made up of the pressure of the dry gas plus the pressure of the water vapour. Thus if a gas, say hydrogen, is collected over water at atmospheric pressure, at 15° C., the height of the barometer being 745 mm., we have the following results:

Height of barometer = 745 mm.
Pressure of moist hydrogen = 745 mm.
Max. tension of water vapour at 15° C. = 13 mm.
Pressure of dry hydrogen 745 – 13 = 732 mm.

These facts, in conjunction with Charles' and Boyle's laws, are of importance in calculating the weight of a gas from its volume, as the weight of 1 litre of the **dry** gas at 0° C. and 760 mm. pressure (normal temperature and pressure or N.T.P.) is a known figure or is easily calculated.

1 litre of dry hydrogen at 0° C. and 760 mm. = 0·0896 grms.

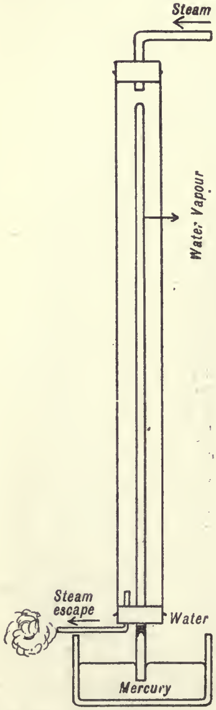

Fig. 11. To show the vapour pressure of water at its boiling point.

Maximum tension of water vapour at its boiling point. The maximum tension of water vapour increases with rise of temperature, and at the boiling point of water is equal to the pressure of the atmosphere, as may be shown with the apparatus illustrated in Fig. 11. In this apparatus the barometric column is surrounded by a wide tube or jacket, containing water into which steam may be passed to raise its temperature, or steam itself may be driven through the wide outer tube to form a steam jacket. As the temperature rises, and as long as water remains permanently on the surface of the mercury, the latter will be depressed. When steam is passed through the outer tube, the vapour pressure in the barometer tube will depress the column of mercury to the level in the trough; as the tube is cooled, the pressure in the tube becomes less and the mercury rises. Actually, with the apparatus as shown in the sketch, the mercury will be driven down the tube approximately to the cork, or approximately the point where the steam makes its exit.

A more compact form of apparatus for demonstrating the same property is shown in Fig. 12, and is described in the following experiment.

Experiment 18. Required: Glass tubing $\frac{3}{16}''$ internal diam., and 12″ long, 500 c.c. wide-mouth conical flask, 2-hole I.R. cork, tripod and burner.

Bend the glass tube into a U-shaped form so that it readily passes into the neck of the flask, and seal the short limb, afterwards inserting the tube through the cork as shown. The short limb is filled with mercury, the latter extending round the bend of the tube, and a drop of water is passed round the bend to the closed end, care being taken to prevent any bubbles of air passing round the bend of the tube. Water is heated in the flask with the tube fixed in position as shown, Fig. 12, and, when steam issues freely through the exit tube in the cork, it will be found that the pressure of the water vapour formed in the closed limb is sufficient to depress the mercury to the level of the mercury in the open limb. The pressure of the water vapour at the temperature of boiling water is therefore equal to the pressure of the external atmosphere.

As already stated, there is a definite maximum tension of water vapour for each temperature, and these will be found tabulated in most analytical works for each degree Centigrade of temperature, for the purpose of obtaining the pressure of a dry gas at any temperature. The following figures are taken from such a table of tensions of water vapour:

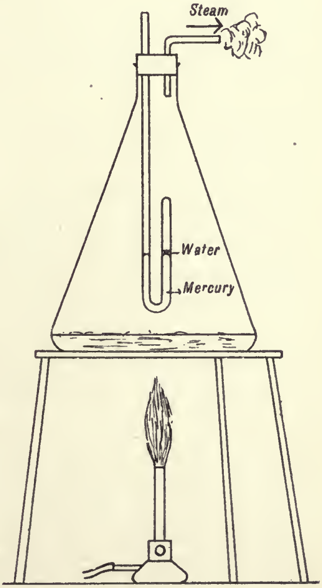

Fig. 12. Apparatus for determination of boiling points.

Temp. C.	Max. Tension of water vapour.
0°	4·6 mm.
10	9·2 mm.
15	12·7 mm.
20	17·4 mm.
30	31·5 mm.
100	760 mm.

(For table of maximum tensions of water vapour at various temperatures, see Appendix.)

The boiling point of a liquid may therefore be defined as that temperature at which the pressure of its vapour is equal to the pressure of the adjacent atmosphere.

CHAPTER III

COMPOSITION OF THE ATMOSPHERE—OXYGEN AND COMBUSTION

ACTION OF METALS AND PHOSPHORUS ON AIR: LAVOISIER'S EXPERIMENT: PREPARATION AND PROPERTIES OF OXYGEN: COMBUSTION: ELEMENTS AND COMPOUNDS.

Action of metals on air.

Many metals when exposed to air, especially if heated, readily undergo a change, and in the case of iron, with which everyone is familiar, the phenomenon, which takes place quickly in moist air, is known as rusting. This is an example of a chemical action, for the metal undergoes a permanent change in properties and in weight.

Experiment 19. Required: Bright iron filings, watch glass, chemical balance and weights, bell jar.

The iron filings are placed on the watch glass and accurately weighed, the watch glass and filings being then put under the bell jar, the sides of which are moistened with water, for several days. On again weighing the watch glass and filings, it will be found that there has been a considerable increase in the weight, and at the same time it will be observed that a brown powder has formed on the surface of the metal.

In order to observe whether any change takes place in the air, the experiment must be carried out with a definite volume of enclosed gas as in the following experiments.

Experiment 20. Required: Iron filings, gas jar, glass dish, ammonium chloride, balance and weights, 100 c.c. graduated jar.

The rusting action takes place much more rapidly in the presence of ammonium chloride solution, and about 10 grams of ammonium chloride are therefore dissolved in about 100 c.c. of water. The inner surface of the gas jar is wetted with the solution, and the filings are shaken up in the wet jar to cause them to stick to the moist surface. The open mouth of the jar is placed in the ammonium chloride solution in the dish and left for some time. Almost immediately, the iron begins to rust, and at the same time the liquid rises in the jar. After a few hours the liquid will be stationary, and if the volume of the liquid, which has entered, is measured, it will be found to be approximately one-fifth of the total volume of the jar. The gas, which remains, will be found to extinguish a lighted taper, and some constituent, which supports the burning of a taper, has therefore apparently been withdrawn from the air.

Similar actions may be brought about with other metals, such as copper, tin, magnesium, etc., which, when heated in free contact with the air, become heavier, and apparently combine with some constituent of the air.

Experiment 21. Required: Hard glass tube about 12″ long, 1-hole I.R. corks to fit tube, glass tubing and I.R. tubing, two measuring cylinders, each 1000 c.c., 2-hole I.R. cork to fit cylinder, pneumatic trough, fan burner or furnace, retort stand and clamp, copper turnings.

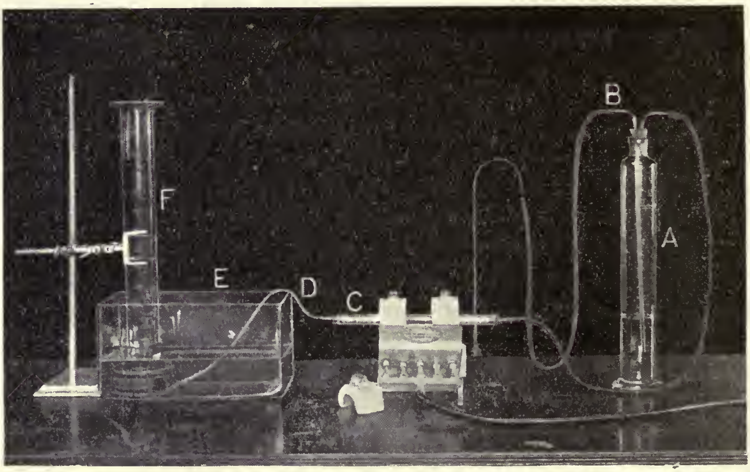

Fig. 13. Showing the composition of the atmosphere by passing a measured volume of air over red-hot copper, and measuring the nitrogen collected.

The apparatus is fitted as shown in Fig. 13, one of the cylinders, *A*, being fitted with bent pieces of glass tubing passing through the cork, one piece, *B*, connected to the water supply, being sufficiently long to reach to the bottom of the cylinder. The hard glass tube, *C*, contains copper turnings, which may be held in position by loose plugs of asbestos wool, and the ends of the tube are fitted with the I.R. corks and glass tubing as shown, the delivery end being connected by a long indiarubber tube, *D*, with the pneumatic trough, *E*. The second cylinder, *F*, is filled with water and suitably supported in the trough. Heat is applied to the tube *C* by means of the fan burner, or a furnace as shown in the sketch, until it is nearly red-hot, and water is then slowly run into the cylinder, *A*, so that not more than one or two bubbles escape from the delivery tube per second, and the escaping gas is collected in the cylinder, *F*.

The volume of the air driven over the copper is represented by the volume of water in *A*, and the volume of gas escaping is measured in *F*. These volumes may be read off from time to time simultaneously, and a series of measurements made. In each case it will be found that the air loses 20°/₀ of its volume in passing over the copper, whilst the copper loses its bright red colour and turns black. The gas collected in the cylinder, *F*, extinguishes a lighted taper.

Action of phosphorus on air.

Other substances, such as phosphorus, which are not metallic, may be used to bring about a similar result.

Experiment 22. Required: Bell jar, pneumatic trough, vertical deflagrating spoon, phosphorus.

The bell jar should preferably be of the form shown in Fig. 14, the neck being closed by a solid rubber cork. The metal spoon, *A*, supported on the metal rod and stand, is termed a vertical deflagrating spoon, and may be used for burning a material in a gas in a vessel such as a bell jar.

The phosphorus, known as yellow phosphorus, must be carefully handled; it is kept under water, as the warmth of the hand is sufficient to cause it to fire. It should therefore always be cut into the pieces required under water, and the pieces then dried with blotting paper, care being taken not to touch it with the fingers after drying.

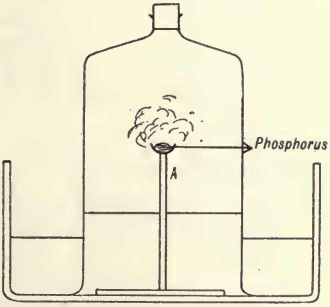

Fig. 14. To show proportion of oxygen in air by burning phosphorus in a measured volume of air.

A small piece of dried phosphorus, about the size of a pea, is placed in the spoon, the bell jar put in position, and, if graduated, the volume of the air is read off. By touching the phosphorus with a hot glass rod, the action may be started and the I.R. cork is immediately put in the neck. The burning action, or combustion, is very vivid at first, but the flame gradually dies down and ultimately is extinguished. White fumes are formed during the combustion, but gradually disappear, and the gas inside the jar becomes clear. A considerable amount of heat is produced in the chemical action, and when the gas has cooled, its volume may be read, after first pouring water into the trough so that the levels inside and outside the bell jar are at the same height. The volumes of air at the commencement and of gas remaining at the end are thus measured under similar conditions of pressure, *viz.* atmospheric pressure, and the final volume is found to be four-fifths of the original volume of air. A more accurate method of carrying out this experiment is the following.

Experiment 23. Required: Long glass tube, ½″ diam., and at least 30″ long, sealed at one end; I.R. cork to fit tube, gas jar, yellow phosphorus.

Several pieces of yellow phosphorus are carefully dried and inserted into the dried glass tube, which is finally tightly corked. By warming the end of the tube gently, the phosphorus is melted and takes fire, and by a sharp tilting motion, the liquid phosphorus may be thrown down the length of the tube. The gas jar is filled with water, and the corked end of the tube is put under the water, the cork being then withdrawn. Water enters the tube, and, when the latter is again at the temperature of the air, the volume of gas remaining will be found to be four-fifths of the original volume of air, if the volume is measured with the levels of the water inside and outside the tube at the same height, as shown in Fig. 15.

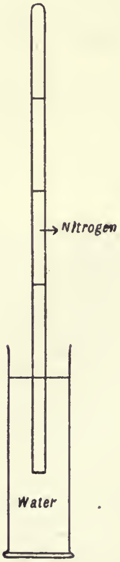

Fig. 15. Composition of air by burning phosphorus in tube with 5 equal divisions.

Lavoisier's experiment.

Lavoisier, in 1774, made use of a similar experiment to obtain a rough idea of the composition of the atmosphere, mercury being heated for several days in a retort, as shown in Fig. 16, in contact with a definite volume of air. The metal was kept at a temperature just below that at which it boils, and gradually became covered with a red powder. At the same time, the air gradually became

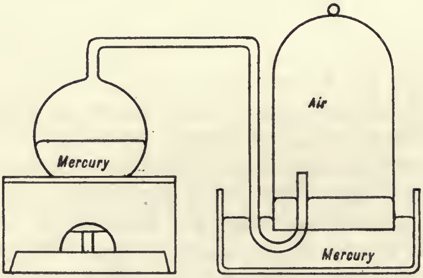

Fig. 16. Apparatus for Lavoisier's Experiment.

smaller in bulk, the total loss in volume being approximately one-fifth of the original volume of the air.

Oxygen—a constituent of the atmosphere. If the red powder, known as mercuric oxide, which is slowly formed on the surface of the mercury in Lavoisier's experiment, is carefully collected, and heated in a glass tube, it is found to give off a gas and mercury is again formed. This gas not only allows a taper to burn in it, but causes it to burn more brightly, and actually rekindles a red-hot splinter of wood. The volume of the gas obtained, which is named **oxygen gas,** is exactly equal to the loss in volume of the air in Lavoisier's experiment, and the oxygen therefore forms one of the constituents of the atmosphere, to the extent of one-fifth by volume. The other principal constituent of the atmosphere is named **nitrogen**; it is the inactive gas obtained in the iron and copper experiments, and forms roughly 80 °/₀ of the air by volume.

Preparation and properties of oxygen.

This production of oxygen from mercuric oxide may be used as a laboratory method for its preparation.

Experiment 24. Required: Hard glass test tube, 1-hole I.R. cork to fit, delivery tube, pneumatic trough, gas jar, retort stand and clamp, mercuric oxide.

The test tube is bent slightly and supported as in Fig. 17, with mercuric oxide placed in the closed end of the tube, which is heated strongly. The solid turns black, and a bright deposit of mercury is formed on the cool sides of the tube, ultimately flowing down into the bend. The oxygen is slowly collected in the gas jar as shown, and may be tested by introducing a glowing splinter of wood into the gas when sufficient is collected.

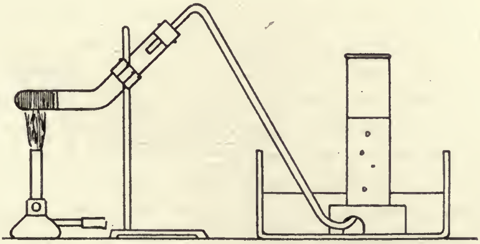

Fig. 17. Preparation of oxygen from mercuric oxide.

Several small jars of the gas may thus be collected, and used for demonstrating some of the more striking properties of oxygen gas.

Experiment 25. Required: Three gas jars filled with oxygen, and covered with greased glass plates, two deflagrating spoons, charcoal, phosphorus, magnesium ribbon.

Copper wire is wrapped round the piece of charcoal to form a wire cage, and this is fixed to one of the deflagrating spoons as shown in Fig. 18. The metal rod of the spoon should be adjusted by sliding it through the cork in the lid, so that the charcoal is about central in the gas jar. The charcoal is made red-hot and then plunged into the oxygen; it glows brightly with the production of sparks, and forms a heavy gas which turns lime water milky. This gas is termed carbon dioxide.

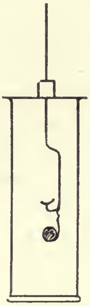

Fig. 18. Burning carbon in oxygen.

A piece of phosphorus is dried, put into one of the spoons, gently heated and plunged immediately into one of the jars of oxygen. An intensely vivid flame is produced, the phosphorus forming white fumes consisting of finely-divided particles of a solid known as phosphorus pentoxide.

The burning of metals may be illustrated by lighting a straight piece of magnesium ribbon, and then plunging it into oxygen. An almost blinding flame is produced, and a white solid, known as magnesium oxide, is formed, similar to the white solid obtained by burning magnesium in air.

Combustion.

These experiments illustrate the most striking property of oxygen, which is its power of supporting the burning or combustion of many common substances; this property is expressed by the term "supporter of combustion," of which oxygen may be considered to be a typical example.

The bodies, which are produced by the burning of metals, and of such substances as phosphorus, carbon, etc., in oxygen, are termed oxides, and these bodies are also formed by the combustion of the same substances in air. In the combustion of common materials, such as coal, wood, etc., in air, the actions taking place are the chemical combinations of the constituents of the substance with the oxygen of the air, generally with the formation of bodies known as oxides.

Elements and compounds.

The substances used or formed in the preceding experiments may be divided into two main classes—elements and compounds.

An **element** may be defined as a body which, up to the present time, has not been broken up into two or more dissimilar substances.

Carbon, phosphorus, sulphur, oxygen, nitrogen, the metals, etc., are examples of the simple bodies known as elements, and no chemical action is known which will break them down into simpler substances.

On the other hand, carbon, phosphorus, etc., combine with oxygen gas to form carbon dioxide, phosphorus pentoxide, etc., and these bodies are obviously more complex; for example, carbon dioxide contains carbon and oxygen. These are examples of compounds, which are produced by the chemical union of elements in definite proportions.

A **compound** may therefore be defined as a substance produced by the chemical combination of elements in certain definite proportions, and which can only be broken up again into its constituents by the agency of a chemical action.

CHAPTER IV

PRELIMINARY STUDY OF WATER—SOLUTION AND CRYSTALLISATION

NATURAL FORMS OF WATER: DISTILLED WATER: PHYSICAL PROPERTIES: LATENT HEATS OF WATER AND STEAM: SOLUTION: SATURATED SOLUTIONS: CRYSTALS AND CRYSTALLISATION: SUPERSATURATED SOLUTIONS.

Natural forms of water.

Water, covering as it does the greater portion of the earth's crust, is the most common liquid and is so well known that a student, commencing the study of chemistry, hardly realises at first the important part that it plays in the science. The natural forms of water may be divided into rain, spring, river and sea water, and it may be noted that this classification, taken generally, denotes the order of purity, rain water being the purest form.

Chemically pure water. The preparation of chemically pure water is a matter of some difficulty. By a process of distillation, the water may be converted into steam and the latter condensed to liquid water again, the solid impurities being left behind in the distilling vessel, so that the water is purified. For all practical purposes, this may be considered to be pure water, or is generally termed distilled water, but prepared in this way such water always contains traces of dissolved gases, and traces of solid matter owing to the action of the water or steam on the glass of the apparatus. To get the water in a perfectly pure form special precautions must be taken and platinum apparatus used.

Preparation of distilled water.

Experiment 26. Required: Distillation flask about 500 c.c. capacity, condenser and indiarubber tubing, 500 c.c. flat or round bottom flask, thermometer and two corks, stands, clamps and bunsen burner.

The apparatus is fitted up as shown (Fig. 19). The corks are fitted to the distillation flask and to the mouth of the condenser respectively, and each is bored, so that the thermometer may be passed through the one fitted to the distillation flask, and the side tube of the distillation flask is passed through the other cork. The bulb of the thermometer is preferably arranged about half an inch below the side tube of the flask, and on no account should it be placed in the boiling water if the true boiling point of the liquid is to be determined. One piece of rubber tubing is connected to the lower side tube of the outer jacket of the condenser and to the water supply, and another piece to the other side tube and the sink. A continuous current of cold water may then be circulated round the inner tube of the condenser, and the steam coming into contact with the cold surface is condensed, the water being collected in the receiving flask. The water should not be boiled too rapidly, otherwise a good deal of spray may be carried over bodily with the steam.

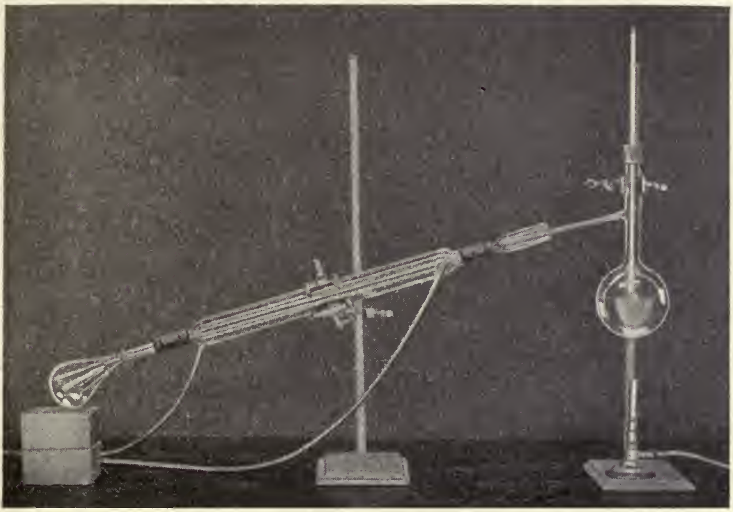

Fig. 19. Preparation of distilled water.

Physical properties of water.

Boiling and freezing points. In the foregoing experiment the mercury in the thermometer rises rapidly at the moment the water commences to boil, and then finally remains stationary whether the water is boiling vigorously or slowly. On a Centigrade thermometer the mercury at this time will mark 100°, and on a Fahrenheit 212°, these being the boiling points of pure water on the respective scales, and these temperatures never vary under normal conditions of pressure.

If, however, the bulb of the thermometer is placed in the water instead of in the steam, the temperature even with pure water may rise several degrees above the boiling point, this being generally accompanied by the explosive boiling known as "bumping." (The bumping may generally be prevented by putting small pieces of broken glass or porous plate into the liquid.) If the water contains dissolved solid matter, it will have a higher boiling point than 100° C. or 212° F., though in all cases under normal conditions the temperature of the steam itself will be 100° C., or 212° F.

A convenient method for determining the boiling point of a liquid is to employ the method described in Chapter II (Fig. 12, p. 21) for showing that at the boiling point the pressure of its vapour is equal to the barometric pressure.

Experiment 27. Required: 12″ glass tube $\frac{3}{16}$″ diam., stand, clamp, beaker, mercury, ether or alcohol.

The glass is sealed at one end and bent into a syphon form, with the closed end forming the short limb as shown in Fig. 12. The closed limb is filled with mercury, and a small drop of the liquid (ether or alcohol) to be tested is passed round the bend into the closed limb, care being taken not to admit air. The tube is then slowly heated in a bath of liquid (water), the boiling point of which is higher than that of the liquid, and ultimately the drop of liquid in the closed end begins to vaporise, the vapour gradually depressing the mercury in this part of the tube. The temperature of the water bath is taken when the mercury in the closed and open limbs stands at the same height; this is the boiling point (B.P.) of the liquid.

If pure water is cooled, it is converted under normal conditions into the solid form, known as ice, at 0° C. or 32° F., though under some circumstances it may be cooled below this point, or be "supercooled," before it freezes. These temperatures are known as the freezing points of water on the respective scales, or the melting points of ice. With solid substances in solution the freezing point is lowered. A steady temperature of 0° C. may be obtained with melting ice.

Maximum density of water. Water, when cooled, contracts in volume, and the density increases until the temperature falls to 4° C., and from this point as the temperature falls it increases in volume and becomes less dense. On being converted into ice there is a still further expansion, and ice is consequently lighter than water at the same temperature. The temperature, 4° C., is known as the **temperature of maximum density of water.**

Latent heats of fusion of ice and vaporisation of water.

In converting ice into water, or in turning water into steam, a considerable amount of heat is required to change the physical state of the substance without altering the temperature; the amount of heat required, expressed in units of heat, to convert unit weight of the substance from one state to the other without change of temperature is termed the latent heat of the body.

The unit of heat commonly employed is the calorie and is the amount required to raise unit weight (1 gram) of water through unit rise of temperature (1° C.).

Experiment 28. Required: Ice, beakers, balance and weights, bunsen burner and Centigrade thermometer.

Cool 120 c.c. of water with ice to about 8° C., and then weigh out from this 100 grams of water in a beaker. At the same time, warm about 120 c.c. of water to approximately 51° C., and weigh 100 grams of water at this temperature. Take the temperature of the two weighed portions, and, when the temperatures are approximately 10° C. and 50° C. respectively, mix the two liquids; the resulting temperature of the 200 grams of water should be 30° C., showing that 100 grams of water in cooling 20° C. have given out a quantity of heat (2000 units) sufficient to raise 100 grams of water through 20° C. rise in temperature.

Experiment 29. Required: As in Experiment 28.

Heat about 120 c.c. of water to 85° C., and then weigh out 100 grams of the liquid. When the temperature of the water has fallen to about 80° C. weigh out quickly 100 grams of ice and mix this with the weighed water. Stir the mixture until the ice is melted and take the temperature, which should be approximately 0° C., thus showing that 100 grams of water in cooling 80° C. have given out sufficient heat (8000 units) to convert 100 grams of ice at 0° C. to water at 0° C. A duplicate experiment may be made with water above 80° C., and it will be observed that the resultant mixture when the ice has just melted is above 0° C.

As 100 grams of ice require 8000 units of heat to convert the solid into liquid without raising the temperature, it follows that unit weight of ice (1 gram), in being converted into water at 0° C., will require 80 units of heat. This is known as the latent heat of fusion of ice.

By a somewhat similar experiment, it may be shown that 1 gram of water at 100° C., in being converted into 1 gram of steam at 100° C., will absorb 537 units of heat, which is termed the latent heat of vaporisation of water.

Solution.

If a substance, such as potassium nitrate or alum, is added to water, the solid gradually disappears and passes into the liquid condition, or is dissolved, and the body is termed a soluble one. The process is known as solution; the water is termed the solvent, and the soluble substance is sometimes named the solute.

This solvent action of water is one of its most striking properties, and for purposes of solution, water is therefore of the greatest importance in chemical and industrial operations.

Substances are generally classed as easily soluble bodies, such as potassium nitrate, salt, etc., insoluble ones, such as calcium carbonate (chalk), silica (sand), etc., and sparingly soluble, such as calcium sulphate (plaster of Paris), the latter class dissolving to a slight extent only in water.

Substances, which—under ordinary circumstances—are the most insoluble, such as silica or sand, may be dissolved to a slight extent by water under suitable conditions of temperature and pressure, and it is doubtful whether there is actually such a body as an insoluble substance. Thus, under the high temperatures and pressures which obtain in the internal portions of the earth's crust, silica may be dissolved by water, as in the geysers of Iceland, and this is deposited from solution when the liquid reaches the surface of the earth. There is good reason to believe that minerals, normally insoluble, occurring in veins in the earth's crust, have in this way been deposited from solution in cavities and cracks in the rocks in which they are found.

Saturated solutions.

When the solid which is being dissolved remains permanently in the liquid, the solution is said to be saturated at the particular temperature of the solvent. This forms a simple method of making a saturated solution, an excess of the solid substance being shaken up with the solvent until the liquid will take up no more of the substance. At the same time, the temperature of the liquid generally falls, this being due to the fact that a certain quantity of heat (latent heat) is required to convert the solid into the liquid condition, and the heat is abstracted from the solvent and surrounding objects.

Experiment 30. Required: Small flask about 100 c.c. capacity, ammonium sulphocyanide, balance and weights, 25 c.c. pipette, thin block of wood.

A striking method of showing the abstraction of heat mentioned above is to dissolve 20 grams of crystalline ammonium sulphocyanide in 25 c.c. of water in a small flask, the latter being placed on a block of wood on which a few drops of water have been placed, and in a few minutes the flask will be frozen to the wood.

As a rule, a saturated solution is no longer saturated if heated to a higher temperature, and more of the solid must be added until again the solid is permanent in the liquid in order to obtain the saturation point. The amount of a substance which can in this way be dissolved by water generally increases very rapidly with increase in temperature, a notable exception being common salt or sodium chloride, which dissolves almost to the same extent in cold water as in hot. The quantity of the solid in grams, which can be dissolved by 100 c.c. of water, or which is required to saturate 100 c.c. of water, is known as the solubility of the substance, and these amounts for different temperatures are generally shown graphically on solubility curves as in Fig. 20.

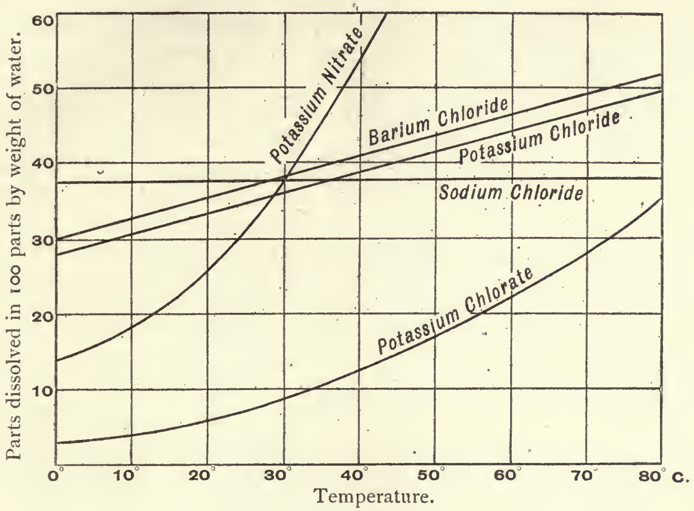

Fig. 20. Solubility curves.

The coordinates in the figure represent temperatures and the number of grams of solid dissolved by 100 c.c. of water respectively, the curves being plotted from the results of experiments.

Experiment 31. Required: Beaker about 100 c.c. capacity, two or three small evaporating dishes, water bath, balance and weights, potassium nitrate, thermometer.

Make a saturated solution of potassium nitrate at about 15° C., and weigh out accurately about 25 c.c. of this clear solution, taking the temperature of the liquid. The liquid may then be evaporated on the water bath, and the weight of potassium nitrate obtained. By deducting this weight from the weight of solution taken, the amount of water required to dissolve the potassium nitrate can be obtained. 1 c.c. of water at 4° C. weighs 1 gram, and it will be sufficiently accurate in this experiment to take this as true at the various temperatures dealt with. By a simple calculation the amount of substance dissolved in 100 c.c. of water can be obtained. The experiment is then repeated, measuring off saturated portions at 30° C., 45° C., and 60° C., cooling before weighing, and the results should be plotted on squared paper. It will be found that the temperature in the latter experiments can be controlled better by placing the beaker containing the solution in another large beaker of warm water.

Plot similar curves for ordinary alum and common salt.

Crystals and crystallisation.

It will be seen from the solubility curves that a substance like alum, or potassium nitrate, is much more soluble in hot water than in cold. Consequently, if a saturated solution is made in hot or boiling water, and the solution then cooled, some of the dissolved substance must separate in the solid condition, the amount separating being shown on the curves by the difference in solubility at the initial and final temperatures of the solution. This process is termed crystallisation, the substance generally separating in well-defined geometrical forms known as crystals; thus salt takes the form of cubes, alum the octahedral form, and copper sulphate in less regular prismatic forms. It will be found, however, that, with each substance, the geometrical forms are uniform, whether the crystals be small or large.

Experiment 32. Required: Large beaker, copper sulphate, tripod, burner, funnel stand, crystallising dish.

About 200 c.c. of water are placed in the beaker and heated nearly to boiling, powdered copper sulphate being added and stirred up with the water until some of the solid is permanent. The liquid, whilst hot, should then be rapidly filtered into the crystallising dish and allowed to cool.

The process of filtration, for removing suspended material, is carried out by folding a circular filter paper, first into a half and then into a quarter circle, one of the folds being then opened so that it has a conical form with three layers on one side and one on the other. In this form it should fit the glass funnel, and it may be fixed in position by wetting it. For rapid filtration, folded filters are sold and may be employed, the paper being opened out and dropped loosely into the funnel. When the liquid is poured into the paper, the latter retains any suspended or insoluble matter and thus a clear solution is obtained.

As the filtered liquid cools, crystals of copper sulphate will separate, and ultimately the liquid (mother liquor) may be drained off, the crystals rinsed with a little distilled water and dried on filter paper. Substances which crystallise in a finely-divided condition are often drained and dried by pressing them on a piece of porous plate.

If the solution contains a small quantity of dissolved substance as impurity, the solution will only be saturated, as a rule, with regard to the copper sulphate, so that normally only the copper sulphate should crystallise. This method may therefore be used to purify a specimen of the commercial compound, known as commercial copper sulphate, the final product being then termed re-crystallised copper sulphate or pure copper sulphate. It should, however, be remembered that a little of the mother liquor may be mechanically enclosed in the crystals, or that the copper sulphate may combine with the impurity to form a double compound, so that this method may not give the absolutely pure compound.

In some cases, several re-crystallisations may be necessary in order to give the pure body.

Water of crystallisation. In many cases the compound takes up water during crystallisation, and this water is not mechanically held but is chemically combined with the substance; it is variously termed water of crystallisation, water of hydration, and in some cases, where it is apparently more firmly held in the substance, water of constitution. The presence of the water, and the loss of the crystalline form caused by its removal, may be shown by the following experiments.

Experiment 33. Required: Crystalline copper sulphate, test tubes.

Heat some small crystals of copper sulphate in a test tube, holding the tube nearly horizontal. Notice the evolution of water vapour and the condensation of water in the cool part of the tube; also that the copper sulphate is turned grey in the process. If the grey copper sulphate is left in contact with water vapour, it again becomes hydrated on cooling and forms the blue crystalline compound.

Experiment 34. Required: Small beaker, glass rod, copper wire, concentrated sulphuric acid, large crystal of copper sulphate.

Wrap the copper wire round the crystal of copper sulphate, and suspend the latter from the glass rod, resting on the beaker containing sulphuric acid, so that the crystal is completely immersed in the acid. The copper sulphate rapidly turns whitish on the outside, and gradually crumbles during a few hours to a grey powder. The concentrated acid has a powerful attraction for the water of crystallisation, combining chemically with it and removing the water from the crystal.

The grey solid copper sulphate, without water of crystallisation, is said to be **anhydrous,** and as it readily combines again with water it is sometimes used for removing water vapour from certain gases, or liquid water from other liquids.

Many compounds take a crystalline form without taking up water of crystallisation, *e.g.*, potassium nitrate, potassium chlorate, etc., and these are termed anhydrous compounds or crystals.

In other cases, a compound may take up definite but varying amounts of water, according to the conditions, either of crystallisation, heat, etc. Thus sodium carbonate crystallises with different amounts of water, according to the conditions of crystallisation, 106 parts by weight of the anhydrous compound taking up either 180, 126, or 18 parts by weight of water. Each of the bodies formed has a distinct crystalline form, and one may pass into the other under suitable conditions. The compound formed with 180 parts by weight of water is the common washing soda, but on exposure to air this gradually parts with nine-tenths of its water and crumbles down to a powder of a different crystalline form. This property of losing water on exposure, due to the vapour pressure of the crystalline hydrate being greater than the vapour pressure of atmospheric water vapour, is termed **efflorescence.**

Other crystalline compounds lose part or the whole of their water on heating. Thus crystalline copper sulphate parts with four-fifths of its water by weight on heating to 100° C., and the whole of its water at 200° C.

This loss of water in many cases results in a change of colour, blue crystalline copper sulphate forming grey anhydrous copper sulphate. An interesting change of colour is shown by the red crystalline cobalt chloride, which turns to the blue anhydrous cobalt chloride on heating. This change has been made the basis for the use of cobalt chloride solution as an invisible ink.

Experiment 35. Required: Cobalt chloride, test tube, camel hair brush.

About 1 gram of cobalt chloride is dissolved in 20 or 25 c.c. of water so as to form a moderately dilute solution, and marks are painted on a sheet of white paper with the liquid by means of the camel hair brush. On drying, the characters will be practically invisible, but, on warming in front of a fire or over a flame, the blue characters become easily visible. On exposure to air, the compound again becomes hydrated by absorption of moisture from the air, and the marks become practically invisible.

If the hydrate has a vapour pressure which is less than that of the atmosphere at the time, it will take up moisture and the compound deliquesces, gradually forming a liquid mass. This property is known as **deliquescence.**

Supersaturated solutions.

In some cases, a hot saturated solution may fail to crystallise on cooling, and in such a case the liquid is over-saturated or supersaturated. The property is somewhat similar to the supercooling exhibited by water, and, as in the case of supercooled water, the liquid is in a very unstable condition. The shaking of the vessel, the entrance of a particle of dust or the addition of a crystal of the substance in solution, will cause immediate and rapid crystallisation. The liberation of a quantity of heat (the latent heat of the substance) through the rapid conversion of the liquid into the solid, causes the temperature of the solution to rise rapidly.

Experiment 36. Required: 1000 c.c. flask, water bath, sodium thiosulphate.

The flask is about half filled with the solid sodium thiosulphate ("hyposulphite"), and the vessel is heated by immersing it in boiling water in the water bath. The compound gradually dissolves (or melts) in its water of crystallisation, and the flask is then allowed to cool slowly, keeping it very still and preventing the entrance of dust by plugging the mouth with cotton wool. When cool, the flask is gently shaken, the plug of wool withdrawn, and, if it still fails to crystallise, a crystal of sodium thiosulphate is added. Crystallisation then rapidly takes place, the temperature rises, and in a few minutes the whole of the substance will be solid.

As the substance immediately crystallises on the addition of a crystal, it follows that a supersaturated solution cannot be formed by cooling the liquid in contact with a crystal of the same substance that is present in the solution. A crystal of the substance in solution is frequently added in processes of crystallisation, with the object of aiding the separation of solid, and preventing the formation of a supersaturated solution, a method known as "seeding" the liquid.

CHAPTER V

COMPOSITION OF WATER—HYDROGEN

ACTION OF METALS ON WATER: PREPARATION AND PROPERTIES OF HYDROGEN: FORMATION OF WATER FROM HYDROGEN: ACTION OF HYDROGEN ON METALLIC OXIDES: ELECTROLYSIS OF WATER.

The action of metals on water.

Many of the common metals will break up water with the liberation of a gas, and these metals may be classified according to the temperature required for the reaction. Thus the three metals, sodium, magnesium and iron may be looked upon as typical of the three groups which break up water at (*a*) the ordinary temperature, (*b*) a gentle heat, (*c*) a red heat.

Preparation of hydrogen.

Experiment 37. Required: Beaker, short wide glass tube, 8″ × ½″, sodium, retort stand and clamp.

When sodium is placed on water, there is a rapid effervescence, with the liberation of a gas which burns and is lighter than air, the gas being named hydrogen. Sodium is a soft metal, easily cut by a knife, showing a bright metallic lustre but rapidly tarnishing in air, and must not be handled if the fingers are moist. It floats on the surface of water, and melts through the heat produced in the chemical action, so that care must be exercised in dealing with it. The heat is not sufficient to cause the hydrogen to fire, unless the water is hot, but accidents have occurred through the use of too large a piece of the metal, and through dropping it on the water from too great a height. Under these conditions, the hydrogen may not only take fire, but may even produce an explosive mixture.

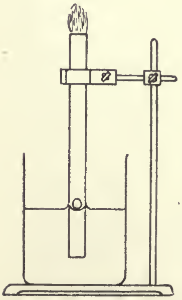

Fig. 21. Action of sodium on water.

A very safe way of showing its action on water is to support the ½″ glass tube, about 8″ long, in the water in the beaker as shown in Fig. 21, and then dropping into the tube a small piece of sodium, which has been moulded in the dry fingers into a small ball. If the glass tube is dry, the sodium will rest on the concave surface of the water, hydrogen gas coming off and rapidly filling the tube. The gas may be lit at the top of the tube, either burning quietly, or exploding slightly if mixed with air; or the gas may be led off from the top by a delivery tube and collected in a test tube over water.

The sodium passes into solution forming a solution of caustic soda (sodium hydroxide or hydrate), which possesses properties known as alkaline; such a solution, *e.g.*, turns red litmus solution or paper to a blue colour, or it will turn a colourless alcoholic solution of phenol phthalein to a strong purple tint. The latter test is the more sensitive one for an alkali, and may be used in this case by adding one or two drops of such a solution to the water.

Experiment 38. Required: 250 c.c. conical flask, 1-hole I.R. cork to fit flask, glass tube to fit cork, I.R. delivery tube, pneumatic trough, tripod and burner, magnesium wire (not ribbon), gas jar.

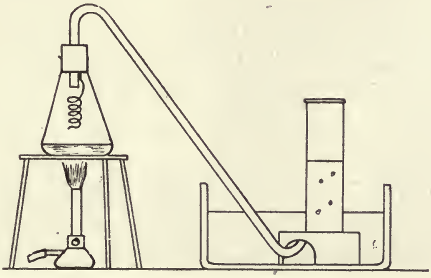

Fig. 22. Magnesium wire burning in steam.

The magnesium wire is coiled into a spiral round a lead pencil, and the end of the wire is nipped between the cork and the delivery tube (Fig. 22). The water in the flask is boiled, and when steam is coming off freely, the wire is lit and lowered into the steam. The cork is held only lightly against the neck of the flask, and is therefore preferably slightly larger than the neck of the flask, the hydrogen being collected over the pneumatic trough. The magnesium is converted into a white oxide, similar to the one formed by burning magnesium in oxygen or in air, and the experiment therefore indicates the presence of oxygen and hydrogen in steam or water.

Experiment 39. Required: Iron tube, ordinary corks, glass and rubber delivery tubes, pneumatic trough, gas jar, furnace, 250 c.c. flask, 1-hole I.R. cork to fit, and iron filings.

The apparatus is fitted up as shown in Fig. 23, the ordinary corks being fitted to the ends of the iron tube and bored to take the delivery tubes. The flask is fitted with the I.R. cork and delivery tube and connected as shown to the iron tube containing iron filings. It is necessary to get a bright red heat otherwise the steam is not decomposed by the iron, and a good gas pressure must therefore be used, and a slow current only of steam is passed when the tube is red-hot. Excess of steam condenses in the water in the trough, and several jars of hydrogen may be rapidly collected. By using a distillation flask as shown, the clip on the rubber tube attached to the glass side tube may be opened, when it is necessary to stop the action.

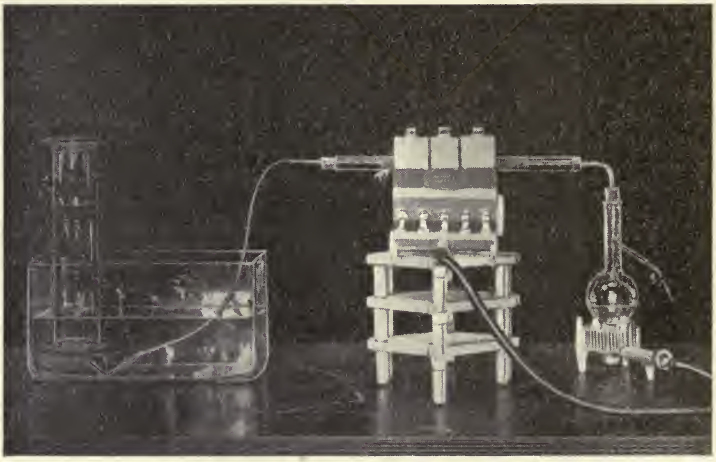

Fig. 23. Preparation of hydrogen by passing steam over red-hot iron.

The iron is converted into a black substance which is magnetic, and which is similar to the iron oxide formed by burning iron wire in oxygen gas, and known as magnetic oxide of iron.

This experiment therefore also indicates the presence of oxygen as well as hydrogen in water, or in steam.

Usual method of preparing hydrogen. A more convenient method of preparing hydrogen is to act on certain dilute acids, such as sulphuric or hydrochloric acid, with zinc, magnesium, iron, etc., and several jars may be rapidly collected for demonstrating the properties of the gas.

Experiment 40. Required: Woulff's bottle (2-necked), thistle tube, two 1-hole I.R. corks to fit bottle, glass tube and I.R. tube for delivery tube, pneumatic trough, gas jars, granulated zinc and dilute sulphuric acid.

The apparatus must be fitted up as shown in Fig. 24, the thistle tube reaching nearly to the bottom of the bottle, and the bent glass delivery tube is passed only just through the cork. A hooked glass delivery tube is connected to the end of the rubber tubing, so as to lead the gas into the inside of the bee-hive shelf, which supports the gas jar for collecting the gas. Granulated zinc is placed in the bottle, and sulphuric acid (dilute) is added through the thistle tube as required. It is of importance to see that there are no possible leakages in the apparatus, which may be tested by pinching the rubber tubing; if the apparatus is tight, the acid will be driven up the thistle tube into the bulb. When the action slackens, more acid may be added through the thistle tube, without opening the bottle and admitting air, sufficient acid being added to give a moderately sharp evolution of gas through the delivery tube.

It is of importance to pay the greatest attention to the following points:

(1) The acid must not be stronger than one volume of acid to four or five volumes of water, otherwise the hydrogen will be mixed with sulphur dioxide gas, which is evolved from moderately concentrated acid when it becomes hot.

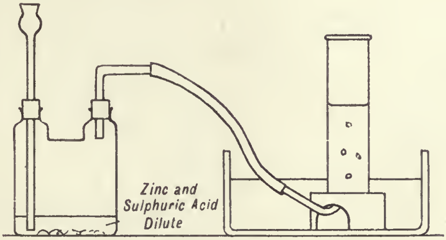

Fig. 24. Preparation of hydrogen.

(2) The gas must be collected at first in a test tube, and then lit at the mouth of the tube. As long as it is mixed with sufficient air it will explode, at first with a sharp but harmless report, and the gas must only be collected in bulk when it has been shown to burn quietly at the mouth of the test tube.

(3) A light must not be placed near the end of the delivery tube, nor must the gas be burnt at the end of the delivery tube, unless a **jar** of the gas has just been collected previously and shown to burn quietly without explosion. If an explosive mixture of hydrogen and air is lit at the mouth of the delivery tube, the apparatus will be blown completely to pieces by a violent explosion.

(4) Each jar, when filled with gas, must be covered by a glass plate, and kept covered **mouth downwards** after withdrawal from the trough, or if the gas has to be kept for some time before use, it is best to stand the jar mouth downwards in a dish of water.

Properties of hydrogen.

(1) The lightness of hydrogen.

Experiment 41. Required: Two glass jars, one filled with hydrogen.

Pour the gas upwards from one jar to the other, as shown in Fig. 1, Chap. I, and show that the gas has risen into the upper jar by applying a light afterwards to both jars.

The fact that hydrogen is lighter than air is sometimes demonstrated by pouring the hydrogen gas into an inverted glass vessel, balanced on a sensitive chemical balance. The vessel containing the hydrogen will rise. (See Fig. 32, p. 52. One of the glass vessels should be inverted.)

Experiment 42. Required: Woulff's bottle, one solid and one 1-hole I.R. cork to fit bottle, short length of glass tubing 4″×½″, 1-hole I.R. corks to fit and short lengths of glass tubing $\frac{3}{16}$″ diameter, calcium chloride and cotton wool, toy balloon and thread, zinc and dilute sulphuric acid.

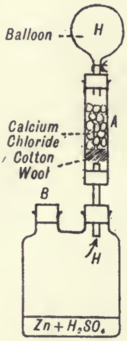

Fig. 25. Filling toy balloon with hydrogen.

The Woulff's bottle is fitted up as shown in Fig. 25, the wide tube, *A*, containing cotton wool and a little calcium chloride for drying the gas, and for trapping spray which is carried forward mechanically in the stream of gas. Zinc and dilute sulphuric acid are placed in the bottle through the neck, *B*, and this is then closed by the solid cork, the gas being allowed to escape for a short period to expel air. The toy balloon is fixed to the outlet by means of thread, and when sufficiently dilated, the neck of the balloon is secured with a little thread. On releasing the balloon, it should readily rise to the ceiling of the room.

(2) Combustibility of hydrogen—non-supporter of combustion.

Experiment 43. Required: Gas jar filled with hydrogen, taper.

Hold the jar of hydrogen mouth downwards, and apply a light. Notice that the gas burns with an almost invisible flame, but that when the lighted taper is thrust into the gas itself, the flame of the taper is extinguished; in such a case the gas is termed a non-supporter of combustion. If, whilst the gas is burning, the mouth of the jar is turned upwards, the gas burns much more rapidly and with a larger flame.

Formation of water from hydrogen.

When dry hydrogen is burnt in air or oxygen, water is formed, and this may be demonstrated by the following experiment.

Experiment 44. Required: Apparatus for preparing hydrogen, retort, stand and clamp, rubber and glass delivery tubes, watch glass, U-tube containing calcium chloride, 1-hole I.R. corks for U-tube fitted with bent glass tubes.

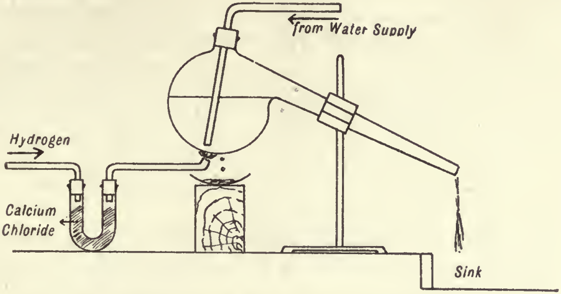

Fig. 26. Formation of water on burning dry hydrogen.

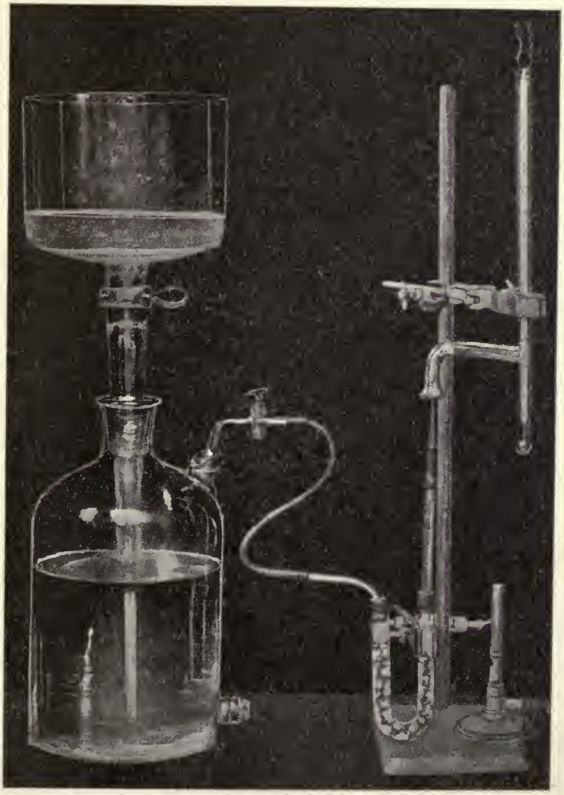

Fig. 27. Formation of water on burning hydrogen.

The delivery tube of the hydrogen apparatus is connected to the U-tube, shown in Fig. 26 (see also Fig. 27), so that the gas is passed over the calcium chloride and dried; care must be taken to expel all the air from the apparatus before lighting the gas. The retort is supported in the clamp so that the outlet tube is over the sink, and the rubber and glass tubes are connected to the water tap so as to deliver water into the bowl of the retort. The watch glass is arranged under the retort, and the hydrogen is lit and burnt in the position shown. Steam is formed and this is condensed by the continuous flow of cold water through the retort, the condensed water collecting in the watch glass.

When sufficient water has been collected, it may be tested by taking its boiling point, or by its action on sodium.

In the apparatus shown in Fig. 27, the hydrogen is contained in a gas holder, passed through a U-tube for drying, and burnt at a fine jet. The steam formed passes into the trumpet-shaped side tube, and into the vertical condensing tube on the right of the diagram. The water collects in the bulb at the bottom, and may afterwards be distilled by a small flame, so as to take its B.P. by the thermometer contained in the vertical condensing tube.

Whenever hydrogen gas is mixed with oxygen or air and lit, water is formed, and the great amount of heat which is developed results in a violent explosion, unless the air or hydrogen is present in very great excess.

Experiment 45. Required: Oxygen, hydrogen, soda water bottle and solid I.R. cork to fit bottle.

Fill the bottle two-thirds with hydrogen, and the remaining one-third with oxygen; the bottle is then corked and several dusters are wrapped round it. On applying a light there is a very violent explosion.

The lightness of hydrogen, its combustibility, and its explosive character when mixed with air, may be shown in a perfectly safe manner by the following experiment.

Experiment 46. Required: Bell jar, glass tube 20″ long by $\frac{1}{4}$″ wide, copper wire.

Bend the glass tube into a siphon form as shown in Fig. 28, and fasten it by means of the copper wire, with the long limb outside the bell jar. Fill the jar with hydrogen through the siphon tube, then disconnect the delivery tube and light the gas at the siphon tube. The fact that the gas can be siphoned out from the vessel shows that it is lighter than air; and the burning of the gas proves it to be combustible. The escape of the hydrogen draws in a corresponding quantity of air into the bell jar, so

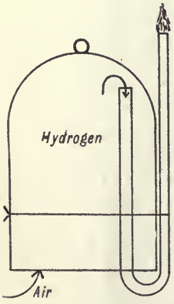

Fig. 28. Siphoning out hydrogen from a bell jar.

that the flame will ultimately flash back and explode the mixture inside with a harmless report. The bell jar may be held in the hand with perfect safety during the experiment, so as to allow free entrance of air.

Action of hydrogen on metallic oxides.

Experiment 47. Required: Hydrogen apparatus, hard glass tube $8'' \times \frac{1}{2}''$, 1-hole I.R. corks to fit, two U-tubes and 1-hole I.R. corks to fit, drying bottle containing sulphuric acid, calcium chloride, balance and weights, glass tubing $\frac{3}{16}''$, fan burner or furnace, black copper oxide.

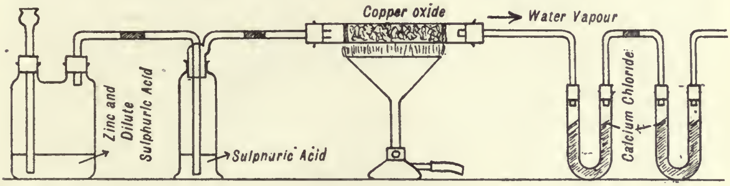

Fig. 29. Formation of water on passing hydrogen over heated copper oxide.

Fit up the apparatus as shown in Fig. 29, the copper oxide being placed in the hard glass tube and held in position by asbestos plugs, whilst the calcium chloride is placed in the U-tubes. The latter, with their delivery tubes, are carefully weighed, and the hard glass tube, with copper oxide, is also weighed.

Hydrogen gas is then passed through the apparatus until all the air has been displaced, and the copper oxide is gradually warmed until it is made red hot. The oxygen in the oxide will combine with the hydrogen gas forming water, and this will be observed condensing on the cool part of the tube, but, by carefully warming the tube, the water may be sent forward in the form of steam into the U-tubes. After about 10 minutes, the tube may be allowed to cool, the hydrogen apparatus disconnected, and the tubes are again weighed.

The decrease in weight of the copper oxide tube will give the amount of oxygen withdrawn, whilst the increase in weight of the U-tubes will give the amount of water formed, and from the difference in these two amounts the quantity of hydrogen combining with oxygen may be found. Calculate the amount of oxygen combining with one part by weight of hydrogen.

In an accurate experiment, it will be found that one part by weight of hydrogen combines with eight parts by weight of oxygen to form nine parts by weight of water.

A few drops of the condensed liquid may be easily collected on a watch glass from the end of the tube containing copper oxide, and by taking the boiling point or by the action of sodium, the liquid may be shown to be water.

The experiment may be repeated with other metallic oxides, such as lead or iron oxides, in order to show that a similar action takes place.

Decomposition of water by the electric current.

When a current of electricity is passed in a suitable manner through water containing a small quantity of sulphuric acid, the water is decomposed, although pure water itself will not conduct the electric current. With a suitable apparatus, the gases evolved may be collected, when it is found that two volumes of hydrogen are obtained for each volume of oxygen.

Experiment 48. Required: Two battery or accumulator cells, or other source of electric current, thin copper wire, large funnel (about 6″ in diameter), two large test tubes, two small pieces of platinum foil (each $\frac{1}{2}'' \times \frac{1}{4}''$), two short pieces of platinum wire (each 2″ long), some paraffin wax and dilute sulphuric acid.

Each platinum wire is welded to a piece of the foil, by placing the two in contact on a smooth metallic surface, and directing a blowpipe flame on to the pieces of metal. Whilst the wire and foil are red hot, they are gently tapped with a hammer, which will cause the wire and foil to weld making a sound joint. The platinum wires are connected to copper wires and the latter fixed in the neck of the funnel by pouring in melted paraffin wax (see Fig. 30), taking great care that the two wires do not come into contact with each other. The whole of the copper wire in the stem of the funnel must be covered with paraffin wax, so as to prevent the copper wire coming into contact with the liquid. The funnel is then filled with water, a little dilute sulphuric acid added, and the test tubes are filled with water and inverted over the pieces of platinum foil. The copper wires are connected to the terminals of the batteries or accumulators, connected in series, and the current passed through the dilute sulphuric acid from one platinum foil to the other.

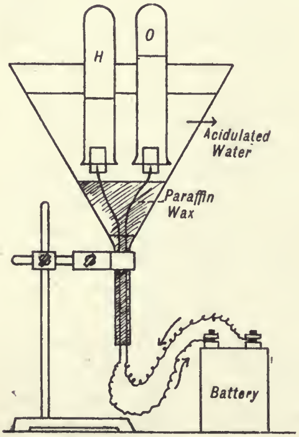

Fig. 30. Decomposition of water by an electric current.

Bubbles of gas will form on the foils, and gradually collect in the inverted tubes. The volume of the hydrogen collected will be found to be twice the volume of the oxygen, and the gases may be identified by the tests already described for hydrogen and oxygen.

The ordinary electric lighting circuit may be used as the source of current in place of the batteries or accumulators, by connecting several electric glow lamps in series with the voltameter as shown in Fig. 31. This apparatus is further described in Chapter XIV, p. 122.

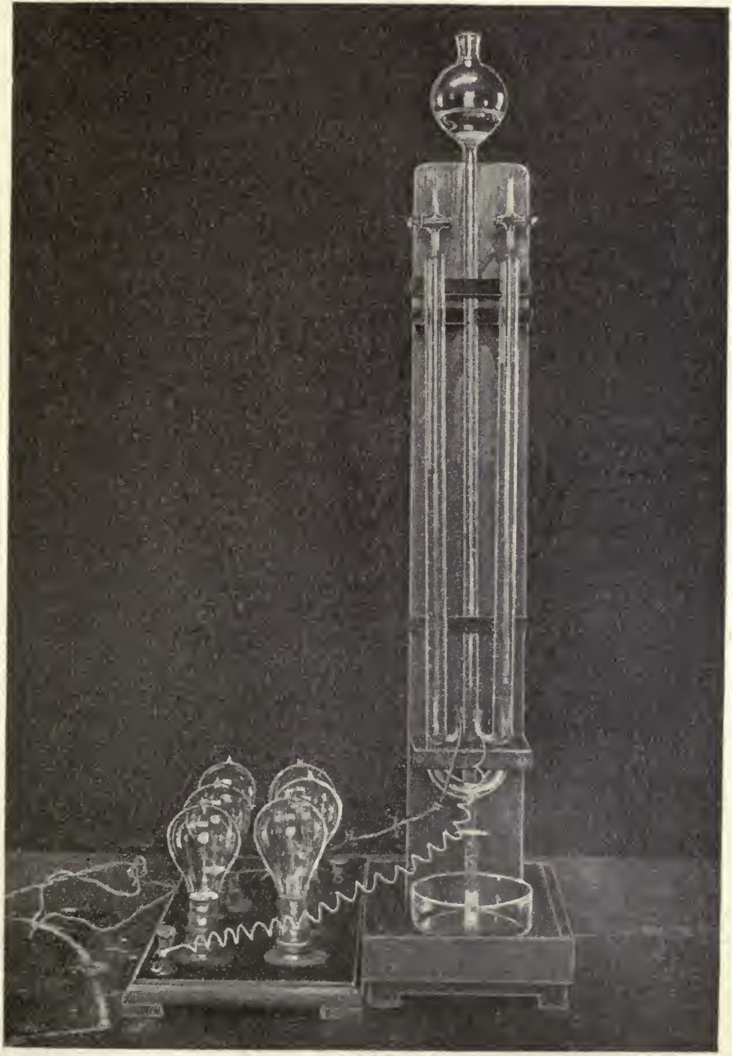

Fig. 31. The Hofmann voltameter for showing electrolysis of water.

CHAPTER VI

PRELIMINARY STUDY OF CARBON DIOXIDE

LIMESTONE: CHALK: MARBLE: LIME: PREPARATION AND PROPERTIES OF CARBON DIOXIDE: COMBUSTION; INDESTRUCTIBILITY OF MATTER.

Limestone, Chalk, Marble and Lime.

Limestone, chalk, and marble, are common constituents of the crust of the earth, and are found in large quantities in the form of masses of rock. Limestone and chalk are used as the source of quick lime, which is obtained from them by a process known as "lime burning." In this process, the limestone or chalk is made red-hot, and then gives off a gas, carbon dioxide gas, leaving behind a solid residue of quick lime.

Marble acts similarly, as in chemical composition it is similar to limestone or chalk, but is a purer substance.

Experiment 49. Required: Porcelain crucible, tripod and pipe clay triangle, bunsen and foot blowpipe, powdered marble, dilute hydrochloric acid, balance and weights.

Weigh out accurately 1 gram of marble in the porcelain crucible and heat it over the bunsen flame till red-hot, maintaining the heat for about 10 minutes, finally keeping it at a red heat for another 5 minutes over a blowpipe flame. When the crucible is cool, again weigh it, and calculate the percentage loss in weight, *i.e.*, the number of grams of gas evolved by 100 grams of the substance. In accurate experiments, the marble will be found to lose 44 per cent. on heating. Some of the original marble and the residue left on heating may be tested by adding in each case a small quantity of dilute hydrochloric acid; it will be found that the marble effervesces rapidly with the acid, whereas the quick lime does not.

Quick lime is slaked, however, immediately it comes into contact with water, generating a great amount of heat, and, if in the form of lumps, it will crumble to a powder, known commonly as "slaked lime." In this form, some of the water has entered into chemical combination with the lime, with the evolution of heat.

Experiment 50. Required: Lumps of freshly-burnt quick lime.

Add a small quantity of water gradually in the form of a fine stream to some large lumps of quick lime, which must either be freshly-burnt, or have been preserved in a tightly stoppered vessel from contact with the outside air for any length of time.

A great quantity of heat will be generated, and some of the water will be converted into steam; the lumps of quick lime will simultaneously crumble.

Quick lime, which has been exposed to the air for some time, is converted gradually into slaked lime, owing to absorption of moisture from the air.

The slaked lime will dissolve to a slight extent in water, forming a dilute solution of "**lime water**," which will be found to be alkaline to litmus or phenol phthalein solutions.

Preparation of carbon dioxide.

Carbon dioxide gas was obtained in the experiments dealing with the properties of oxygen, by burning charcoal in oxygen gas, and it is generally formed when substances containing carbon, such as wood, coal, coke, coal gas, oil, petrol, etc., burn in oxygen or air.

It is evolved also from nearly all carbonates, when they are exposed to a red heat, as already observed in the cases of limestone, chalk and marble, which are forms of calcium carbonate.

The usual method of preparing a quantity of carbon dioxide, however, is to act upon calcium carbonate with dilute hydrochloric acid, as mentioned in Experiment 49 above. The action, when using lumps of marble, is not so furious and is more easily regulated than with a powdered form of calcium carbonate, and marble is therefore generally used for the preparation.

Experiment 51. Required: Apparatus similar to the one used for the preparation of hydrogen, lumps of marble, dilute hydrochloric acid.

The marble is broken up into small pieces and placed in the Woulff's bottle, dilute hydrochloric acid being added to keep up a steady evolution of gas, which is collected over the pneumatic trough, as in the preparation of hydrogen. Several jars of gas may be collected, and closed with glass plates with the mouths of the jars upwards.

Properties of carbon dioxide.

(1) Action on a lighted taper.

Experiment 52. Required: Jar of carbon dioxide, taper.

Plunge a lighted taper into the jar of gas, and notice that the flame is extinguished. About 3 per cent. of carbon dioxide in air is sufficient to extinguish a flame, such as that of a taper or candle.

(2) Weight of the gas.

Experiment 53. Required: Two gas jars, one filled with carbon dioxide.

Pour the gas slowly downwards into the jar containing air; show by means of a lighted taper that the whole of the gas escapes from the upper jar, and that at the end of the experiment the lower jar contains carbon dioxide.

The gas may be shown to be heavier than air by pouring it into a glass vessel, balanced mouth upwards on a sensitive chemical balance as in Fig. 32.

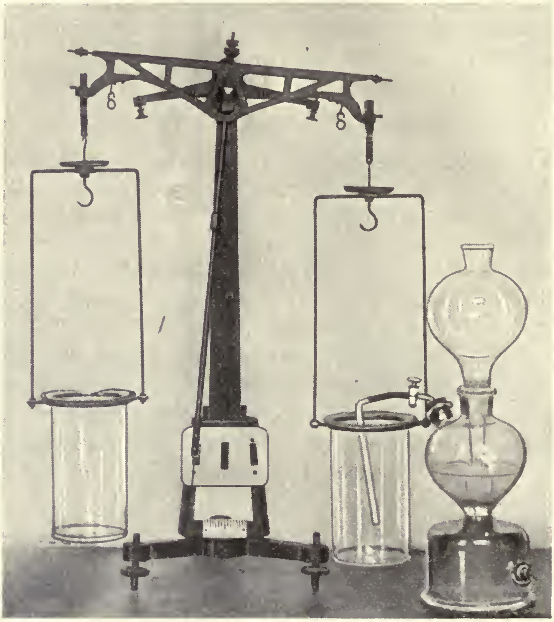

Fig. 32. To show that carbon dioxide is heavier than air by weighing on a sensitive chemical balance.

(3) **Action on lime water.**

Experiment 54. Required: Gas jar containing carbon dioxide, lime water.

Add a small quantity of lime water to the jar of carbon dioxide, and shake the gas with the liquid. The lime water will be turned milky, owing to the formation of insoluble calcium carbonate, which remains suspended in the liquid. This is the test commonly applied for carbon dioxide gas.

Combustion.

Chemical actions taking place in the burning of a candle, taper, coal gas, petrol, oil, etc. From the knowledge already gained of the composition of carbon dioxide and water, it is now possible to investigate the chemical actions taking place in the burning of a candle, or other substance, similar in composition, such as petrol, etc.

Experiment 55. Required: Deflagrating spoon, short piece of candle, two gas jars, one containing oxygen.

Fix the short piece of candle in the spoon by means of melted wax, light the candle, and allow it to burn in the jar of air. In a short time, the flame will begin to flicker, and will finally be extinguished. On adding lime water to the gas, the liquid will be turned milky.

Repeat the experiment using the jar of oxygen, and a similar action will take place, the flame in this case shrinking in size, though much brighter than in the case of air. As the action in the case of pure oxygen is taking place more rapidly, a greater quantity of heat is being developed in a definite time than with air; consequently a higher temperature is obtained and the wax of the candle is rapidly melted.

These actions, in conjunction with the burning of carbon in oxygen, demonstrate that in the burning of the candle, carbon is combining with oxygen in the air with the production of carbon dioxide gas.

Experiment 56. Required: Bell jar, wood cork to fit, long narrow glass tube, candle, 2 thin blocks of wood.

The long glass tube is passed through the cork, which is fitted to the bell jar, and the latter is supported on two blocks of wood over the burning candle as shown in Fig. 33. The wood blocks allow air to enter the bell jar, so that the candle will continue to burn, and the products of the combustion are carried in the upward draught of gas into the long condensing tube. Drops of liquid are obtained, and, by catching one or two drops on a watch glass, sufficient may be obtained to show, from the determination of its B.P., and its action on a small piece of sodium, that the liquid is water.

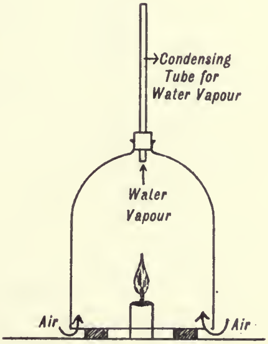

Fig. 33. Condensation of water formed by the burning of a candle.

It therefore appears that hydrogen must be combining with oxygen to form water. We may infer from these experiments that the candle, petrol, etc., must contain carbon and hydrogen, and that when these substances are burnt in air or oxygen, their constituents combine with the oxygen to form carbon dioxide gas and water vapour.

Indestructibility of matter.

In the burning of a candle, although the matter apparently disappears, yet we have seen that it reappears in other forms, namely, as gases, one of which is heavier than air. The matter of the candle has not been destroyed, and this is characteristic of all chemical actions—**matter is**

indestructible. In order to show that the whole of the matter from the candle may be accounted for, the following experiment may be made.

Experiment 57. Required: Wide glass tube 12″ long by 2″ wide (a straight glass lamp chimney is suitable), wire gauze, copper wire, 2″ ordinary corks, short piece of candle, granular calcium chloride, soda lime, large tubulated bottle, corks to fit, glass tubing, balance and weights.

A round piece of wire gauze is cut to fit the lamp chimney, and is suspended by the copper wire, so as to form a kind of basket for the support of the granular calcium chloride and soda lime, which are mixed in the upper part of the chimney. The upper end is then fitted with cork and delivery tube. The candle is supported on a thin strip of cork, which is cut away to form several large holes for the entrance of air, and the cork is fitted to the lower part of the tube. The tube, including cork, candle, calcium chloride, soda lime, and delivery tube, is then carefully weighed.

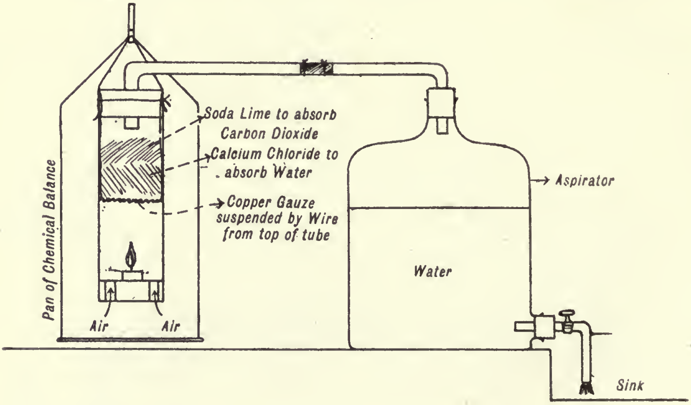

Fig. 34. Indestructibility of matter.

The tubulated bottle, fitted up as shown in Fig. 34, and containing water, is connected to the apparatus, so that by running out the water from the bottle, it acts like an aspirator drawing a current of air through the tube. The candle is lit, and burnt for two or three minutes, the current of air being regulated by the speed of the water so that the candle is kept burning. After cooling, the tube is again weighed, when it will be found to have gained in weight. This is due to the oxygen of the air combining with the constituents of the candle, and the products of the combustion are absorbed by the substances in the upper part of the tube; the whole of the original candle is still in the tube, but in the form of absorbed gases (carbon dioxide absorbed by the soda lime and water vapour absorbed by the calcium chloride) which have been formed by the chemical union of the carbon and hydrogen of the wax and wick of the candle with the oxygen of the air.

CHAPTER VII

ELEMENTS AND COMPOUNDS—SYMBOLS, FORMULAE AND EQUATIONS—LAWS OF CONSTANT, MULTIPLE AND RECIPROCAL PROPORTIONS

ELEMENTS AND COMPOUNDS: METALS AND NON-METALS: SYMBOLS: EQUIVALENT WEIGHT: LAWS OF CONSTANT, MULTIPLE AND RECIPROCAL PROPORTIONS: ATOMS: DALTON'S ATOMIC THEORY: KINETIC THEORY AND MOLECULES: ATOMIC AND MOLECULAR WEIGHTS: FORMULAE: EQUATIONS.

Elements and compounds.

The division of all substances into elements, or simple bodies, and compounds was briefly dealt with in Chapter III (p. 28); the substances which are known as mixtures also fall within this classification, as they are either mixtures of elements or compounds, or both. The bodies, known as alloys, may be either mixtures of metals or compounds of metals combined in certain definite proportions.

Metals and non-metals. For many purposes, it is convenient again to classify the elements, of which there are about 70 known, into metals and those which do not possess metallic properties, or non-metals.

Of the non-metals, there are about 20 known, and of the metals about 25 are common, the remainder being known as rare metals.

The properties, commonly termed metallic properties, are hardness, weight, lustre, conduction of heat and electricity; but it is not possible by means of these properties to obtain a perfect classification, and a far more satisfactory one is found in the basic character of the metals, which will be dealt with in Chapter X (p. 83). It may, however, be said that as a rule a metal will be heavy, hard, possess a high lustre and will readily conduct heat and electricity.

Symbols. These consist of a letter or letters used to represent a definite weight of an element, the first letter being a capital, and the second letter, if one is used, a small one. As a general rule, when several elements commence with the same letter, the most common of these has the single letter, though this must not be taken as invariable.

LIST OF COMMON ELEMENTS, CLASSIFIED AS NON-METALS AND METALS, WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

	Names of elements	Symbols	Atomic weights
	Non-metals.		O = 16
	Hydrogen	H	1·008
	Oxygen	O	16
	Sulphur	S	32·07
	Selenium	Se	79·2
	Tellurium	Te	127·5
	Nitrogen	N	14·01
	Phosphorus	P	31·04
	Boron	B	11·0
	Carbon	C	12·00
	Silicon	Si	28·3
Halogens	Fluorine	F	19·0
	Chlorine	Cl	35·46
	Bromine	Br	79·92
	Iodine	I	126·92
	Helium	He	3·99
	Neon	Ne	20·02
	Argon	A	39·88
	Krypton	Kr	82·9
	Xenon	X	130·2
	Metals.		
	Sodium (Natrium)	Na	23·00
	Potassium (Kalium)	K	39·1
	Copper (Cuprum)	Cu	63·57
	Silver (Argentum)	Ag	107·88
	Gold (Aurum)	Au	198·2
	Magnesium	Mg	24·32
	Calcium	Ca	40·09
	Strontium	Sr	87·63
	Barium	Ba	137·37
	Zinc	Zn	65·37
	Cadmium	Cd	112·40
	Mercury (Hydrargyrum)	Hg	200·0
	Aluminium	Al	27·1
	Tin (Stannum)	Sn	119·0
	Lead (Plumbum)	Pb	207·10
	Arsenic	As	74·96
	Antimony (Stibium)	Sb	120·2
	Bismuth	Bi	208·0
	Chromium	Cr	52·0
	Manganese	Mn	54·93
	Iron (Ferrum)	Fe	55·85
	Nickel	Ni	58·68
	Cobalt	Co	58·97
	Platinum	Pt	195·2
	Osmium	Os	190·9
	Iridium	Ir	193·1

The symbols are commonly derived from the English name, but in the case of common metals, known to the early chemists, they have been in most cases derived from the Latin name which is shown in brackets in the preceding list of elements. The first letter of the English or Latin name is used for the symbol, and if a second letter is employed, one of the following letters in the name, frequently, though not always, the second letter.

Equivalent weight.

In the chapter on water, p. 47, it was shown that, in forming water from hydrogen and copper oxide, one part by weight of hydrogen combines with eight parts by weight of oxygen. By actual experiment, it has been shown that a definite weight of each element will always combine with or replace one part by weight of hydrogen; this is termed the **equivalent weight** of the element. With many metals, this may be determined by dissolving a definite weight of the metal in acid, measuring the volume of hydrogen liberated, and then calculating the weight of dry hydrogen obtained.

Experiment 58. Required: Hempel's burette, 250 c.c. conical flask, 1-hole I.R. cork to fit, glass and I.R. tubing for delivery tube, specimen tube $3'' \times \frac{3}{4}''$, magnesium ribbon, concentrated hydrochloric acid, stand and clamp, thermometer and barometer, balance and weights.

The apparatus is fitted up as shown in Fig. 35, and the measuring tube of the burette is filled with water to the tap by raising the pressure tube. A piece of magnesium ribbon (about 0·07 gram) is weighed off accurately, and placed in the flask with a little water, concentrated hydrochloric acid being placed in the specimen tube and carefully lowered into the position shown in the flask, taking care not to allow any of the acid to escape into the water. The cork is fitted tightly to the flask and the delivery tube connected to the burette. The tap of the latter may now be opened, and the flask is tilted so as to allow the acid to flow out of the tube into the water. Chemical action at once begins, the metal dissolves and hydrogen is liberated, the displaced gas passing into the burette. When the action is at an end, the apparatus is left for a few minutes for the gas to come to the temperature of the room, and the pressure tube is adjusted till the levels of water in both pressure tube and measuring tube are at the same height. The volume of gas may then be read off, the temperature of the room and the height of the barometer being simultaneously taken.

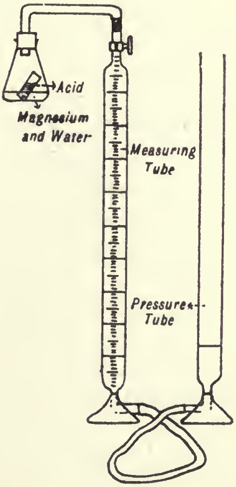

Fig. 35. Determination of equivalent weight.

The calculation is then made in the following manner:

Weight of magnesium wire taken = 0·067 gram.
Volume of gas obtained (hydrogen) = 70 c.c.
Temperature = 16·5° C.
Barometer = 746 mm.
Tension of water vapour at 16·5° C. = 13·95 mm.
∴ Pressure of dry hydrogen = 746 − 13·95 = 732·05 mm.
70 c.c. of dry H obtained at 16·5° C. and 732·05 mm.

Correcting by Charles' and Boyle's Laws, we get:

Volume of H at 0° C. and 760 mm. pressure

$$= \frac{70 \times 273 \times 732{\cdot}05}{289{\cdot}5 \times 760} = 63{\cdot}5 \text{ c.c. (approximately).}$$

1000 c.c. of dry H at 0° C. and 760 mm. pressure = 0·0896 gram.

63·5 c.c. ,, ,, ,, $= \frac{0{\cdot}0896 \times 63{\cdot}5}{1000}$ gram.

∴ $\frac{0{\cdot}0896 \times 63{\cdot}5}{1000}$ gram of H are displaced by 0·067 gram of Mg.

1 gram of H will be displaced by $\frac{1000 \times 0{\cdot}067}{0{\cdot}0896 \times 63{\cdot}5} = 11{\cdot}8$ grams of Mg.

∴ 11·8 = equivalent weight of magnesium.

The equivalent weights of other metals, such as zinc, aluminium, etc., may be determined in a similar manner.

Other methods of determining equivalent weights. There are many other methods of determining equivalent weights of metals, but the principal ones may be classified thus:

(1) By passing hydrogen over an oxide of the metal.
(2) By displacement of one metal by another.
(3) By combining oxygen with the metal.

These methods are dealt with in sequence in the experiments detailed below.

Experiment 59. Required: Apparatus for passing H over black copper oxide as described in Experiment 47.

Weigh off accurately about 2 grams of powdered copper oxide and place it in the hard glass tube, which is then carefully weighed. The calcium chloride tubes are also accurately weighed.

After connecting the various parts, the air is entirely displaced from the apparatus by hydrogen, and the copper oxide is gradually heated until it is finally red hot, the heat being maintained until the black oxide is entirely converted into red metallic copper.

The copper oxide tube, after cooling, is again weighed, thus giving the loss of weight, which is oxygen, and by deducting this from the weight of copper oxide taken, the weight of metallic copper will be obtained. The calcium chloride tubes are also weighed to obtain the weight of water formed in the experiment.

Then calculate the weight of O which combines with 1 part by weight of H, and this will be the equivalent weight of oxygen = 8.

By calculating the weight of the metal (copper in this case) which was united with 8 parts by weight of oxygen, the equivalent weight of the metal will be obtained. As all the metals combine under suitable conditions with oxygen gas, this method of calculating the equivalent weight of a metal from the equivalent weight of oxygen is frequently employed.

Experiment 60. Required: Metallic copper or granulated tin, porcelain dish, tripod and gauze, balance and weights, concentrated nitric acid, funnel to fit inside the dish to cover it.

About 1 gram of metallic tin is accurately weighed off in the porcelain dish, covered with a little water and about 5 c.c. of concentrated nitric acid added, the dish being covered by the funnel. A vigorous action takes place, and when the action is at an end, a little more nitric acid is added if any of the metal still remains. Finally the solution is gently heated in a fume cupboard carefully to drive off the excess of acid and water, the residue of tin oxide being finally strongly heated and weighed. Having found the weight of tin oxide obtained from the weight of tin taken, calculate the amount of tin combining with the E.W. (8) of oxygen.

In the case of copper, copper nitrate is formed, but this is converted into copper oxide on heating strongly.

Experiment 61. Required: Magnesium powder, solid silver nitrate, 100 c.c. beaker, balance and weights.

About 0·2 gram of magnesium powder is weighed off accurately in the small beaker, and about 4 grams of silver nitrate dissolved in 50 c.c. of water added to the magnesium. The mixture is stirred well, the magnesium gradually dissolving and displacing metallic silver from the solution. After about 1 hour, pour off the liquid, wash the residue several times by adding water and carefully draining off the liquid, taking care not to pour away any of the metal. The metal in the beaker is finally dried in an oven, or by gently heating over a flame, and then weighed.

Example: Weight of Mg powder = 0·207 gram.
,, silver obtained = 1·832 grams.

$$\therefore \text{ 12 grams of Mg replace } \frac{1 \cdot 832 \times 12}{0 \cdot 207} = 106 \cdot 2 \text{ grams Ag.}$$

$$106 \cdot 2 = \text{E.W. of Ag.}$$

Laws of chemical combination.

Law of Constant Proportions. Quantitative experiments, made in this way by determining the equivalent weights of the elements, show that for any one compound the composition is always constant. Thus, it has been stated that water may be formed by passing hydrogen over a great number of metallic oxides, such as copper, lead, iron, etc., but in all cases it is found that one part by weight of hydrogen combines with 8 parts by weight of oxygen to form 9 parts by weight of water. Similarly, copper oxide may be formed by passing oxygen over red-hot copper, or it may be formed, as already stated above, by acting on metallic copper with nitric acid and then strongly heating the compound which is formed. In each case, by taking a definite weight of copper, it may be shown that 31·78 grams of copper combine with 8 grams of oxygen to form black copper oxide.

These facts are expressed in the form of a law, known as the **Law of Constant Proportions**, which states that "The **same compound** is always made up of the **same elements** united together in the **same proportion.**"

Elements with more than one equivalent weight—Law of Multiple Proportions. Some metals are found to combine with oxygen or other similar elements in more than one proportion, for example, copper, tin, lead, iron, etc., form more than one oxide each, and each metal in the different oxides has a different equivalent weight. Copper, *e.g.*, forms two oxides, the red oxide and the black oxide of copper.

In the black oxide of copper, it is found that the copper combines with oxygen by weight in the following proportion:

$$\mathrm{Cu} : \mathrm{O} = 31{\cdot}78 : 8.$$

In the red oxide of copper:

$$\mathrm{Cu} : \mathrm{O} = 63{\cdot}56 : 8.$$

Similarly, the equivalent weight of tin is found to be 59·5, when the tin is dissolved in dilute hydrochloric acid, and the volume of hydrogen evolved is measured; whereas, when the tin is dissolved in concentrated nitric acid to combine the metal with oxygen, the equivalent weight of the metal is found to be 29·75. This is again due to the fact that tin may combine with oxygen in more than one proportion, and it will be observed in each of the above examples, that the higher equivalent weights are simple multiples of the lower.

This leads us to another law, known as the **Law of Multiple Proportions**, which states that "When two or more elements combine together in more than one proportion, the higher proportions of one element, combining with a fixed proportion of the second element, are simple multiples of the lower proportion."

Example: Two oxides of nitrogen have the following percentage composition:

	1st Oxide	2nd Oxide
Nitrogen	63·65 per cent.	46·68 per cent.
Oxygen	36·35 "	53·32 "

In the first oxide:

36·35 parts by weight of O unite with 63·65 parts by weight of N.

1 part by weight of O unites with $\frac{63·65}{36·35} = 1·751$ parts by weight of N.

In the second oxide:

53·32 parts by weight of O unite with 46·68 parts by weight of N.

1 part by weight of O unites with $\frac{46·68}{53·32} = 0·875$ parts by weight of N.

$$\frac{1·751}{0·875} = \frac{2}{1} \text{ (approximately).}$$

Law of Reciprocal Proportions. By the analysis of various compounds of the elements, the **Law of Reciprocal Proportions** has been established; this states that "If two elements, *A* and *B*, each separately combine with a third element, *C*, the proportions of *A* and *B* which combine with the same proportion of *C*, are those in which *A* and *B* will combine together."

Thus hydrogen will combine with chlorine and iodine in the following proportions by weight:

$$\text{H} : \text{Cl} = 1 : 35·5.$$
$$\text{H} : \text{I} = 1 : 127.$$

It is found that iodine and chlorine will combine together to form a compound, iodine monochloride, and this combination takes place in the following proportions by weight:

$$\text{Cl} : \text{I} = 35·5 : 127.$$

Atoms—Dalton's atomic theory. In order to explain the various facts enumerated above, Dalton formulated the theory which is commonly known as **Dalton's atomic theory**, which supposes that all elements are made up of extremely minute particles, termed **atoms**, the original meaning of which was a particle which was **indivisible.**

Although we know now that there must be even smaller particles than Dalton's "atoms," yet the theory still holds good in supposing that there is in each element a definite minute portion, which is the atom, and which is the smallest particle of the element entering into, or displaced from, a chemical compound.

Dalton's atomic theory may be briefly summarised thus:

(1) Each element is made up of an extremely large number of minute particles, which are termed atoms.

(2) The atoms of any one element are the same in shape, size and weight, but differ in weight, and may be different in shape and size, from those of other elements.

(3) The relative weights of the atoms of the different elements are termed the atomic weights.

Kinetic theory and molecules. The various laws, which have been dealt with already, such as Charles' and Boyle's Laws, and also the

Law of Diffusion of Gases to be dealt with later, may be explained on the assumption that matter is not continuous but is grain-like in structure. These minute particles are in continuous and rapid movement, the volume of each particle being very small in comparison with the size of the spaces between them, and in the case of hydrogen gas it has been estimated that the particles are moving with an average velocity of over 1400 metres per second. Some of the particles will momentarily come to rest by collisions with the sides of the vessel or with one another, whilst others may be moving temporarily at a higher velocity than the average. The pressure of a gas on the sides of a vessel is due to the continuous bombardment of these particles, and by compressing the gas the spaces only are diminished, and consequently the number of bombardments per unit of time is increased, which gives rise to a corresponding increase in pressure.

These minute particles, which are capable of separate existence and independent movement, are termed molecules, and all bodies whether element or compound are made up of molecules, each molecule moving independently as a separate particle. The molecules of a liquid have a much more limited movement than those of a gas, and in the case of a solid are more restrained still.

Atomic and molecular weights. Methods have been devised, which cannot be dealt with at the present stage, for determining the weights of the atoms relative to an atom of hydrogen, and also the weights of the molecules relative to a molecule of hydrogen. The atomic weights of the common elements are given on p. 56, but as the atomic weight of oxygen enters very largely into the determinations of other atomic weights, $O = 16$ is now taken as the standard instead of $H = 1$ in the list of "international atomic weights."

The atomic weights of hydrogen, oxygen, nitrogen, carbon, sulphur and certain other common elements are commonly taken in round figures, thus $H = 1$, $O = 16$, $N = 14$, $C = 12$, $S = 32$.

The molecular weights of the elements and compounds may be also determined experimentally by methods which will be dealt with later, and we obtain for some of the common elements the following series of figures:

Element	Atomic weight	Molecular weight	Molecule
Hydrogen	1	2	H_2
Oxygen	16	32	O_2
Nitrogen	14	28	N_2
Sulphur	32	256	S_8
Phosphorus	31	124	P_4
Mercury	200	200	Hg
Zinc	65	65	Zn

From figures such as the above, it has been shown that many of the common elements contain two atoms in each of their molecules, or are diatomic, others are more complex still, whereas in other cases they are monatomic, such as mercury, zinc, argon, helium, etc.

In the cases of elements with more than one atom in their molecules, the latter must be broken up by heat or other means into atoms before chemical action can begin between the elements, as chemical action only takes place between the various atoms, and as already stated the atom is the smallest particle of an element which enters into combination, or which is displaced from a chemical compound.

Exothermic and endothermic compounds. In the formation of compounds from elements, heat is, as a rule, evolved, or the reaction is said to be **exothermic**, the number of units of heat evolved in the formation of the molecular weight of the compound being known as the **heat of formation.** In other cases, however, heat may be absorbed, as in the combination of hydrogen and iodine to form hydriodic acid, and the reaction is then said to be **endothermic.** This is due to the fact that more heat is required or absorbed in breaking up the individual molecules of the elements into atoms, before chemical action can begin, than is afterwards evolved in the combination of the atoms to form the compound.

It may be noted that the structure of the molecules of some elements has not been determined, but may be known to be very complex as in the case of carbon ; in such cases the element is not represented in molecula form, but is always written in the form of the symbol.

Formulae.

In the determination of the equivalent weight of oxygen, it has been shown that one part by weight of hydrogen combines chemically with eight parts by weight of oxygen to form nine parts by weight of water. As the atomic weight of oxygen is 16, and this is the smallest proportion which can enter into chemical combination, we have :

weight of H combining : weight of O combining : : 2 : 16.

The simplest formula which can be given to a molecule of water is therefore

$$\overset{H_2O}{\overset{\diagup \quad \diagdown}{\underbrace{2 + 16}_{18}}}$$

which represents that 2 parts by weight of hydrogen combine with 16 parts by weight of oxygen to form 18 parts by weight of water ; this agrees with the molecular weight of steam, or water, which is found to be 18*.

Formulae are used in this manner to represent the molecules of elements or compounds, the symbols of the elements in a compound being written side by side, and a small figure placed after each one to represent

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* There is reason for believing that under some conditions the formula for water may be more complex than this, though the formula is commonly written H_2O.

the number of atoms of that element present in the molecule. When only one atom is present, no figure is used, and in considering the formula of a compound or a symbol of an element, it should always be understood that a symbol stands for a definite weight represented by the atomic weight of the element.

We can now see why tin, copper, etc., under certain conditions, may each have two equivalent weights, *e.g.*, in the black oxide of copper :

$$\text{weight of Cu combining : weight of O combining} = 31{\cdot}78 : 8 \\ = 63{\cdot}5 : 16;$$

in the red oxide of copper :

$$\text{weight of Cu combining : weight of O combining} = 63{\cdot}5 : 8 \\ = 2 \times 63{\cdot}5 : 16.$$

As the atomic weights of copper and oxygen are 63·5 and 16 respectively, we obtain for the two formulae :

Black oxide of copper or cupric oxide = CuO
Red oxide of copper or cuprous oxide = Cu_2O

Similarly the composition of other compounds is determined from analysis, and from a knowledge of the composition, the equivalent and atomic weights of the elements and the molecular weights of the compounds, we are able to arrive at a definite formula for each compound, and in the following pages these will be used without giving the reasons to show how they have been arrived at. For example in sulphuric acid :

$$\text{weight of H : weight of S : weight of O} = 1 : 16 : 32.$$

Atomic weights of H = 1, S = 32, O = 16 ; molecular weight of sulphuric acid = 98.

Therefore in the molecule of sulphuric acid we have :

$$\text{weight of H : weight of S : weight of O} = 2 : 32 : 64,$$

or the formula becomes

$$\begin{array}{c} H_2 \quad S \quad O_4 \\ / \qquad | \qquad \backslash \\ (2 \times 1) + 32 + (4 \times 16) \\ \underbrace{2 + 32 + 64}_{98} \end{array}$$

In some formulae, some of the groups of elements have to be doubled, trebled, etc., in amount, and this may be represented either by placing a large figure in front of the group or by putting a small figure outside a bracket. Thus copper nitrate may be represented $Cu\,(NO_3)_2$ or $Cu\,2NO_3$, though the former method is more commonly used, as the large figure "2" following the Cu may be easily taken for a small figure referring to that element. Both the formulae shown represent one atom of copper, two atoms of nitrogen, and six atoms of oxygen. **Great care** should therefore be taken in writing formulae, so that there is no doubt as to what is meant, and in the case of a small figure following a symbol, the figure should be small, near to the symbol and slightly below it.

Equations.

Chemical reactions are represented whenever possible by chemical equations, these being a collection of symbols or formulae grouped together to show the substances taking part in the reaction, and also the substances which are formed.

The substances combining together are placed on the left side of the equation, the substances formed on the right side, and the two sides are separated by an arrow* pointing in the direction that the reaction takes.

Thus, zinc when dissolved in dilute sulphuric acid liberates hydrogen gas and there is left a solution of zinc sulphate ($ZnSO_4$) in the preparing vessel; this is represented:

$$\begin{array}{ccccccc} Zn & + & H_2SO_4 & \rightarrow & H_2 & + & ZnSO_4 \\ \text{zinc} & & \text{sulphuric acid} & & \text{hydrogen} & & \text{zinc sulphate} \end{array}$$

Each substance in an equation should be written in true molecular form, thus when mercuric oxide is heated it splits up into mercury and oxygen, but if we wish to represent the reaction in a molecular form, the following equation would not be strictly correct:

$$HgO \rightarrow Hg + O$$

In some cases, a reaction may be conveniently represented by the simplest form of equation, as in the example above, but it is more correct in this case to double the reaction throughout so as to represent the oxygen in molecular form. In representing more than one molecule of a compound, a large figure is placed in front of the formula, thus:

$$2HgO \rightarrow 2Hg + O_2$$

In putting the equation into words, we may state that mercuric oxide when heated "yields" (instead of "equals") mercury and oxygen.

This, however, is not sufficient, as we ought also to state that "two molecules of mercuric oxide when heated yield two molecules of mercury and one molecule of oxygen."

In addition, the equation represents the proportions by weight in which the reaction takes place, thus:

$$\begin{array}{ccccc} 2HgO & \rightarrow & 2Hg & + & O_2 \\ / \quad \backslash & & | & & | \\ 2(200 + 16) & & \underbrace{2\times 200} & & \underbrace{2\times 16} \\ | & & & & \\ \underbrace{2\times 216} & & 400 & & 32 \\ 432 & & & & \end{array}$$

So that in order to put the reaction above completely into words, we state, in addition, that "432 parts by weight of mercuric oxide when heated yield 400 parts by weight of mercury and 32 parts by weight of oxygen."

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* The sign "equals" (=) is frequently used in place of the arrow, but is not so satisfactory, as one side is not actually equal to the other. A triple line (≡) has also been suggested, but the arrow is probably most satisfactory, as the double arrow is commonly used in balanced actions (see p. 89).

PART II

SYSTEMATIC STUDY OF THE NON-METALS AND THEIR IMPORTANT COMPOUNDS, MORE PARTICULARLY THOSE USED IN THE TEXTILE INDUSTRIES

NOTE:—*In the succeeding chapters, in order to save some space in the descriptive matter, the work has not been plotted out as definite experiments, but the student should pick out the portions which are suitable for experimental illustration with the apparatus at his command, and these experiments should be carefully carried out.*

With the experience already gained, the student should now be able to dissect an experiment, and readily find out what is required for fitting up any particular piece of apparatus.

CHAPTER VIII

HYDROGEN—REDUCTION AND REDUCING AGENTS—DIFFUSION

Preparation and properties of hydrogen: Reduction and reducing agents: Nascent condition: Diffusion: Graham's law of diffusion.

Preparation and properties of hydrogen.

Hydrogen: Symbol, H; Atomic weight, 1.

Occurrence. Hydrogen may be shown to be present in the free state in the earth's atmosphere, but only to a very slight extent, and similarly in the solid crust of the earth it is found in only a limited amount. It occurs chiefly in nature in the form of water, one-ninth of the liquid by weight consisting of hydrogen. By analysis of the light emitted from the sun and the stars, it has been shown that the atmospheres of these bodies contain large quantities of hydrogen.

Preparation. (1) Hydrogen gas may be obtained, as already described in Chapter V, from water or from steam by the action of certain metals. Sodium, potassium, and calcium decompose water at ordinary temperatures; zinc, magnesium, aluminium, etc., when gently heated decompose steam, and iron, nickel, and cobalt, at a red heat, similarly liberate hydrogen from steam, the following chemical actions taking place:

$$2Na + 2H_2O \rightarrow \underset{\substack{\text{caustic soda}\\ \text{or}\\ \text{sodium hydroxide}}}{2NaOH} + H_2$$

$$Mg + H_2O \rightarrow MgO + H_2$$

$$3Fe + 4H_2O \rightarrow \underset{\substack{\text{magnetic oxide}\\ \text{of iron}}}{Fe_3O_4} + 4H_2$$

(2) Hydrogen may also be liberated from the alkalis, caustic soda and caustic potash, which are formed as shown above by the action of the metals on water, by the further action of sodium or potassium, zinc or aluminium on the substances. Thus, if zinc or aluminium foil is heated with a strong solution of sodium or potassium hydroxide, hydrogen is liberated:

$$2NaOH + Zn \rightarrow \underset{\text{sodium zincate}}{Na_2O, ZnO} + H_2$$

(3) The most convenient method for the preparation of hydrogen is the action of dilute hydrochloric acid or sulphuric acid on metals, such as zinc, aluminium, tin, iron, nickel, cobalt, magnesium. In some cases, *e.g.*, with tin, the action takes place more readily on heating gently, but with zinc, magnesium, iron, etc., the action goes on readily in the cold. With magnesium and dilute hydrochloric acid, pure hydrogen may be obtained, and, although the hydrogen is not pure when obtained from granulated zinc and dilute acid, owing to certain impurities present in the metal, it is sufficiently so for most practical purposes, and this is the method generally used. It has already been described in detail in Chapter V. The hydrogen obtained from dilute acid and metallic iron is very impure, and generally has an odour of oil or grease. The following actions take place in these cases:

$$Zn + H_2SO_4 \rightarrow H_2 + \underset{\text{zinc sulphate}}{ZnSO_4}$$

$$Fe + H_2SO_4 \rightarrow H_2 + \underset{\text{iron sulphate}}{FeSO_4}$$

$$Mg + 2HCl \rightarrow H_2 + \underset{\text{magnesium chloride}}{MgCl_2}$$

It may be noted that hydrogen is not obtained by the action of nitric acid on metals, with the exception of magnesium, which liberates hydrogen from very dilute nitric acid (1 vol. of acid and about 12 vols. of water).

Properties. Hydrogen is a colourless, tasteless, odourless gas, only very slightly soluble in water; it is lighter than air and is the lightest substance known. It is a non-supporter of combustion, but is combustible in air or oxygen, burning with an almost invisible pale blue flame and forming water when burnt. Hydrogen is sometimes said to be the best fuel, as in the combustion of unit weight of the element, with the formation of water, there is produced a greater quantity of heat than in the combustion of unit weight of any other element, 1 gram of the gas forming 34,200 units of heat during its combustion. When mixed with air or oxygen, it forms an explosive mixture, 2 volumes of hydrogen combining with 1 volume of oxygen to produce steam or water. Experiments have already been described (Chapter V) to demonstrate the above properties of the gas.

Reduction and reducing agents.

Reduction is an important chemical action, and has already been illustrated in Exp. 47, in which hydrogen gas is passed over red-hot copper oxide with the production of metallic copper and water. This may be looked upon as a typical reducing action, and hydrogen may be considered to be a typical reducing agent.

Most of the compounds formed by the combination of metals with oxygen may be reduced in a similar manner to the metallic state by means of hydrogen gas, or other similar reducing agent. The action consists essentially in the withdrawal of oxygen from a compound by means of the reducing agent, producing either the metal or a compound containing a lesser amount of oxygen; other elements, however, may be similarly withdrawn, or even a group of elements from a compound, and the action is still known as reduction. For example, iron forms several oxides, two of which are known as ferrous oxide (FeO) and ferric oxide (Fe_2O_3), the latter being termed a higher oxide and the former a lower oxide; corresponding to these oxides, there are two series of compounds of iron, known as ferrous and ferric compounds, which will be described more in detail in Chapters X and XI, examples of these being ferrous chloride ($FeCl_2$) and ferric chloride ($FeCl_3$), ferrous sulphate ($FeSO_4$) and ferric sulphate $\{Fe_2(SO_4)_3\}$. These higher compounds may be reduced by hydrogen to the lower ones by the withdrawal either of the non-metal, or the group of elements, combined with iron, *e.g.*, oxygen, chlorine, or sulphion group (SO_4). This is illustrated in the following equations:

$$\underset{\text{ferric oxide}}{Fe_2O_3} + H_2 \rightarrow H_2O + \underset{\text{ferrous oxide}}{2FeO}$$

$$\underset{\text{ferrous oxide}}{FeO} + H_2 \rightarrow H_2O + \underset{\text{iron}}{Fe}$$

$$\underset{\text{ferric chloride}}{FeCl_3} + H \rightarrow \underset{\text{ferrous chloride}}{FeCl_2} + HCl$$

$$\underset{\text{ferric sulphate}}{Fe_2(SO_4)_3} + 2H \rightarrow \underset{\text{ferrous sulphate}}{2FeSO_4} + H_2SO_4$$

All these actions are known as reduction, and a **reducing agent** may therefore be defined as a substance which will withdraw oxygen, or an element or group of elements similar to oxygen, from a compound.

Other important reducing agents are carbon, carbon monoxide, sulphuretted hydrogen, etc.

These actions are of the greatest importance in chemical work, the metals for example being generally obtained from mineral substances or from compounds by reduction, and many actions in textile work are reducing actions, *e.g.*, bleaching by sulphur dioxide, etc.

Nascent condition.

The term "nascent" means "being born," and is applied to the condition of an element or a substance at the moment it is liberated from a compound, at which time it is in a more active condition. Hydrogen, for example, at the instant it is liberated from sulphuric acid or from another compound, will be momentarily in the form of atoms, which must either combine with atoms of other elements, or the atoms will combine with one another to form molecular hydrogen. Whilst it is in the form of "atomic hydrogen" it is much more active chemically, and is then said to be in the "nascent state," or is termed "nascent hydrogen."

The difference between molecular hydrogen and nascent hydrogen may be shown by the action of a solution of ferric chloride or sulphate. When bubbled through such a solution, hydrogen (*i.e.* molecular hydrogen) is without action on the substance in solution, but if the hydrogen is liberated in the solution itself, *e.g.*, by the addition of zinc and sulphuric acid to the liquid, it will rapidly bring about a chemical change. In this case, the atoms of hydrogen combine with either the chlorine to form hydrochloric acid, or with the SO_4 (sulphion) group to form sulphuric acid.

This reducing action of nascent hydrogen is illustrated in the equations shown above, in which the hydrogen is shown in the nascent condition by representing it in the form of atoms instead of in the molecular condition. The change taking place is rendered obvious by the change in colour of the solution, which turns from a yellow or yellow-brown tint to an almost colourless one.

Such actions are also of the greatest importance in chemistry, as many changes may be brought about by a substance in the nascent state, which would otherwise not be possible under the ordinary molecular conditions.

Diffusion.

Hydrogen is lighter than air, and in the experiments already described it has been stated that the jars of gas must be held mouth downwards to prevent the escape of the hydrogen. If a jar of the gas, however, is freely exposed to the air with its mouth downwards, it is impossible to keep the gas indefinitely in the jar, as owing to the rapid movement of the molecules of the hydrogen, the latter will gradually escape and mix freely with the air, until in about 15 minutes it is impossible to detect the presence of hydrogen in the jar by means of a light.

This property of mixing with another gas, even in opposition to its density, is known as diffusion, and is common to all substances, solids, liquids, and gases, being simply due to the movement of the molecules of the substances. It is much more evident with gases than with liquids or solids, owing to the greater freedom of movement of the molecules of gases, and is more easily demonstrated with hydrogen than with other gases because of its lightness and consequent greater average velocity of its molecules.

It is this property which causes an escape of coal gas in a room, even near to the ceiling, to be detected in every part of the room by the odour of the gas, and once the gases have been thoroughly mixed they do not separate again according to their relative densities, but remain as a uniform mixture owing to the continuous movement of the molecules. The atmosphere, *e.g.*, contains several gases mixed together, which are always kept thoroughly mixed by the process of diffusion.

In the case of gases, the process takes place through the most minute orifices, such as a crack in a vessel, or through the pores of filter or blotting paper. This may be shown by filling an inverted gas jar with coal gas, and placing this mouth to mouth with a jar of air, the two jars being separated by a piece of blotting paper; in about 15 minutes the coal gas may be detected in both jars by the application of a light. At the same time, it should be noticed that whilst the coal gas has been passing downwards into the air, the latter is also making its way upwards into the coal gas, and that some of the molecules may wander backwards and forwards from one jar to the other. The action in fact will go on until a perfect mixture of coal gas and air is obtained, and even then diffusion still takes place from one jar to the other.

Graham's diffusiometer. This property of diffusion of gases was investigated in detail by Graham by means of a simple apparatus known as Graham's diffusiometer, shown in Fig. 36, which consists essentially of a long glass tube closed at one end by a plug of plaster of Paris. The lower end of the tube is narrower, so as to act as an index tube for showing the rise of a liquid such as coloured water, and for this purpose may, if necessary, be furnished with a graduated scale. The porous plug is covered by a tin foil cap held in position by a rubber band, and the tube is filled with hydrogen by displacement, the lower end of the tube being then put down into a trough of coloured water and the tin foil cap removed. Diffusion at once commences, hydrogen passing to the outside through the porous plug, and air passing to the inside of the tube, but as the hydrogen diffuses out quicker than the air can enter, the coloured liquid rises in the tube. This proves that hydrogen diffuses more quickly than air. A similar experiment may be made by filling the tube with coal gas, or other gas which is lighter than air, or a gas heavier than air, such as carbon dioxide, may be employed. In the latter case, some of the carbon dioxide should be sucked out of the tube by inserting a narrow piece of rubber tubing through the water into the gas after placing the diffusiometer in position, so as to draw the coloured liquid into the tube. On removing the tin foil cap and allowing diffusion to proceed, the air will diffuse into the tube quicker than the carbon dioxide can make its exit, and the coloured liquid will be driven down the tube.

Fig. 36. Graham's diffusiometer.

By employing a graduated scale, and allowing diffusion to proceed with different gases for a definite length of time in each case, an idea of the relative rates of diffusion may be obtained.

Graham's law of diffusion of gases. In this way, Graham measured the rates of diffusion of various gases, and showed that these follow a definite law, which may be stated thus: "The relative rates of diffusion of different gases, under similar conditions of temperature and pressure, are inversely proportional to the square roots of their vapour densities."

Vapour density of a gas. The vapour density of a gas is the number of times the gas is heavier than an equal bulk of hydrogen, measured under similar conditions of temperature and pressure. The vapour density of hydrogen is taken as unity, and, as oxygen is 16 times as heavy under similar conditions of temperature and pressure, the vapour density (V.D.) of oxygen is 16. From the law of diffusion of gases we therefore obtain:

$$\begin{array}{lll} \text{V.D. of H :} & \text{V.D. of O} & = 1 : 16 \\ \text{Rate of diffusion of H :} & \text{Rate of diffusion of O} & = \sqrt{16} : \sqrt{1} \\ & & = 4 : 1 \end{array}$$

thus showing that hydrogen will diffuse exactly four times as rapidly as oxygen under similar conditions of temperature and pressure.

Other experiments for illustrating diffusion of gases. The apparatus shown in Fig. 37 may be used for illustrating that hydrogen diffuses more rapidly than air. *A* is a porous pot, such as is used in a Leclanché battery cell, which is tightly closed with a 1-hole rubber cork fitted with a long glass tube. The latter passes through a cork into a Woulff's bottle containing coloured liquid, and the second neck of the bottle is fitted with a glass tube drawn out at the outer end into a fine jet.

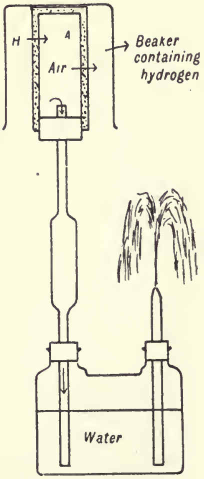


Fig. 37. Apparatus to demonstrate that hydrogen diffuses more quickly than air.

Diffusion will be taking place continually through the pores of the pot, air entering and leaving the vessel, but if the pot is surrounded by a large beaker or bell jar filled with hydrogen, the latter will diffuse into the pot quicker than the air can leave it. The excess of gas passes down into the Woulff's bottle, and, exerting a pressure upon the coloured liquid, will drive out the water through the jet tube in the form of a fountain.

On withdrawing the bell jar containing hydrogen, the hydrogen now inside the pot will diffuse out into the outer air quicker than the air can enter, and the coloured liquid is drawn up towards the porous vessel.

A similar experiment may be made with carbon dioxide, the Woulff's bottle being replaced by a bent glass tube containing coloured water, acting as a manometer tube, as shown in Fig. 38. When the porous vessel is surrounded by an atmosphere of carbon dioxide, the air will diffuse out of the pot quicker than the carbon dioxide can enter, and the consequent reduction in pressure in the vessel will draw the coloured liquid towards the porous pot. On removing the beaker containing carbon dioxide, the carbon dioxide inside the pot will diffuse out, but more slowly than the air can enter, and the increased pressure in the vessel drives the coloured liquid away from the porous vessel.

The presence of carbon dioxide in the porous vessel may be shown, after diffusion has been going on for some little time from the atmosphere of carbon dioxide into the pot, by disconnecting the latter and pouring the gas into a gas jar containing a little lime water, which will rapidly be turned milky.

Several applications have been made of this important property, *e.g.*, in the partial mechanical separation of gases of different densities, detection of a foreign gas in the atmosphere, etc.

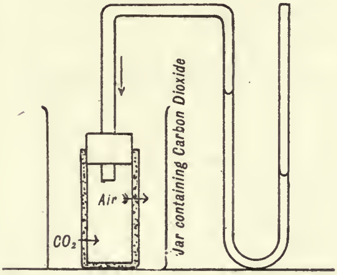


Fig. 38. Apparatus to demonstrate that air diffuses more quickly than carbon dioxide.

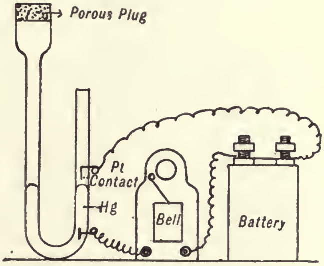


Fig. 39. Apparatus for detecting the presence of a gas lighter than air.

The apparatus shown in Fig. 39 has been used to detect the influx of fire damp into the atmosphere of a coal mine, and in principle is exactly similar to the one shown above in Fig. 37, the coloured liquid being replaced by mercury which forms part of an electric bell circuit. In this case the passage of fire damp (or coal gas may be used in the actual experiment) through the porous plug, drives the mercury round the bend of the tube until it comes into contact with the platinum wire, thus completing the circuit and the bell rings. When the fire damp is removed from the vicinity of the apparatus, the fire damp, which has diffused into the apparatus, gradually escapes from the vessel through the porous plug quicker than the air can enter, and the electrical circuit is again broken.

The textile student will find many applications of this property of diffusion in the drying of substances, in the removal of water vapour by diffusion into the outer atmosphere, and in other similar phenomena, for example, in the conditioning of wool, etc., where moist air must be brought by some suitable means, such as diffusion, into contact with the material.

CHAPTER IX

OXYGEN—OXIDES—OXIDATION AND OXIDISING AGENTS

PREPARATION AND PROPERTIES OF OXYGEN: MANUFACTURE OF OXYGEN: OXY-HYDROGEN, OXY-COAL GAS AND OXY-ACETYLENE FLAMES: OXIDES, OXIDATION AND OXIDISING AGENTS.

Preparation, manufacture, properties and uses of oxygen.

Oxygen: Symbol, O; Atomic weight, 16.

Occurrence. Oxygen is the most abundant of all the elements, for as already described one-fifth of the atmosphere by volume, and eight-ninths of water by weight consist of oxygen, whilst 50 per cent. of the earth's crust by weight also consists of this element. In the latter case the oxygen is largely in combination with the element silicon and with the metals as oxides.

Preparation. (1) Oxygen may be obtained from certain metallic oxides by the action of heat, and its preparation from mercuric oxide (HgO) has been already described (Exp. 24).

It may also be obtained by heating black manganese dioxide to a dull red heat in a hard glass test tube, the oxygen being collected in the usual way over water; in this case only one-third of the oxygen is evolved as a gas and a residue of trimanganic tetroxide (or the brown oxide of manganese), Mn_3O_4, is left, thus:

$$3MnO_2 \rightarrow Mn_3O_4 + O_2$$

(2) Pure oxygen is best obtained by heating potassium chlorate, $KClO_3$, which breaks up into potassium chloride and oxygen. The compound is heated in a hard glass test tube, first crackling and melting, and then evolving a steady stream of pure oxygen, which may be collected over water, or over a trough of dry mercury if required dry. The following action takes place:

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

(3) A better method of obtaining a supply of oxygen for laboratory purposes, and the one generally used, is to heat a mixture of potassium chlorate with about one-fourth of its weight of manganese dioxide in a dry

flask as shown in Fig. 40. The oxygen is not pure, but contains small quantities of chlorine, though it is sufficiently pure for most purposes.

The flask is supported with the neck pointing downwards, so that any moisture which condenses in the neck of the flask will flow downwards towards the delivery tube, and away from the hot body of the flask.

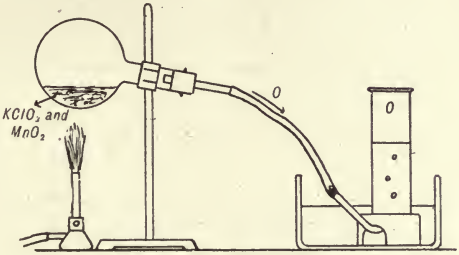


Fig. 40. Preparation of oxygen.

A gentle heat only is required, and a very rapid stream of oxygen is obtained at a temperature not sufficient to melt the potassium chlorate, the whole of the oxygen being obtained from the potassium chlorate whilst the manganese dioxide is unchanged during the process. The action may thus be represented by the following equation, although it is probable that certain secondary reactions take place between the potassium chlorate and manganese dioxide, with re-formation of practically the whole of the manganese dioxide.

$$2KClO_3 + MnO_2 \rightarrow 2KCl + 3O_2 + MnO_2$$

Catalysis and catalytic agents. Many examples, such as this, are known in chemical work, in which a substance is used to aid or to start a reaction, without itself being changed. Such an action is known as catalysis, and the body, which brings about the reaction without being changed itself, is known as the catalytic agent.

Manufacture of oxygen. (4) Until quite recently, oxygen was obtained on a manufacturing scale from the air by a method known as the **Brin's oxygen process**, in which barium monoxide is first heated for some time at a dull red heat in contact with purified air under pressure, the current of air being afterwards stopped and the heating continued under reduced pressure. In contact with air, the barium monoxide combines with oxygen forming barium peroxide, thus :

$$2BaO + O_2 \rightarrow 2BaO_2$$

Under reduced pressure, the barium peroxide is again broken up into barium monoxide and oxygen, the evolved gas being stored in gas holders, and then compressed into steel cylinders, generally under a pressure of 120 atmospheres.

$$2BaO_2 \rightarrow 2BaO + O_2$$

Such a reaction, which may be made to take place in either direction according to the particular conditions, is often termed a reversible reaction and may be represented thus :

$$2BaO + O_2 \rightleftarrows 2BaO_2$$

This method of manufacturing oxygen has now been almost entirely replaced by electrolytic methods of obtaining oxygen from water ; or by methods of obtaining oxygen from liquid air, in which case the air is liquefied by great cold and pressure, and the nitrogen is separated from the oxygen by a process of distillation, the lower boiling point of the liquid nitrogen causing it to distil away, leaving liquid oxygen in a moderately pure condition.

Properties. Oxygen is a colourless, odourless, tasteless gas and is very slightly heavier than air, so that it may be collected by downward displacement if required dry, though it is preferably collected over water. It is very slightly soluble in water, and the aeration of drinking water is largely due to dissolved air, which is, to a large extent, dissolved oxygen. The gas may be liquefied by great cold and pressure, the boiling point of liquid oxygen being $-180°$ C. ; so-called "liquid air" is largely liquid oxygen.

The most striking property of oxygen is its power of supporting the combustion of substances which burn in air, and this property has already been referred to in Chapter III. A red-hot splinter of wood bursts into flame if put in the gas, a property which is commonly made use of as a test for moderately pure oxygen.

The non-metals, phosphorus and sulphur, if previously lit, and carbon (or charcoal) if made red-hot, burn brilliantly in pure oxygen, producing white fumes of solid phosphorus pentoxide (P_4O_{10}), or gaseous sulphur dioxide (SO_2), or carbon dioxide (CO_2), the following actions taking place :

$$P_4 + 5O_2 \rightarrow \underset{\text{phosphorus pentoxide}}{P_4O_{10}}$$

$$S + O_2 \rightarrow SO_2$$

$$C + O_2 \rightarrow CO_2$$

By the addition of water to the products of the above actions, the substances dissolve and acids are produced, the resultant liquids turning blue litmus solution or paper to a red tint.

Similarly, metals may be made to combine directly with oxygen gas ; sodium, magnesium, zinc, aluminium, iron wire, etc., burning brilliantly in oxygen if previously heated or lighted in a suitable manner.

Sodium may be heated in a deflagrating spoon and plunged into the oxygen, thus forming solid sodium peroxide :

$$2Na + O_2 \rightarrow Na_2O_2$$

Magnesium ribbon or wire may be lighted and simply plunged into oxygen, forming a dazzling white flame, which is rich in the rays affecting a photographic plate.

$$2Mg + O_2 \rightarrow 2MgO$$

Aluminium is best burnt in oxygen in the form of leaf; two or three leaves of aluminium are pushed into a jar of dry oxygen, and a very small piece of red-hot charcoal is dropped on to the metal by means of crucible tongs. There is an almost blinding flash, and the oxygen combines with the metal with the formation of solid white aluminium oxide (or alumina), Al_2O_3.

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

This action is the basis of the one taking place in the use of "thermit," a substance which is used commercially for welding iron. This body consists of an intimate mixture of ferric oxide (Fe_2O_3) and powdered aluminium, and when sufficiently heated by a red-hot piece of metal, or if lit by burning magnesium ribbon or powder, a vigorous chemical action takes place, the aluminium combining with the oxygen and liberating metallic iron.

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$$

The mass becomes white hot, and sufficient heat is produced to keep the liberated iron in a molten condition for several minutes. The action may be shown quite safely in an earthenware dish, such as is used in metallurgical work, and the "thermit" may be lit by a magnesium ribbon fuse supported in a small heap of magnesium powder, the molten iron being poured out into sand when the combustion is finished.

Oxy-hydrogen, oxy-coal gas and oxy-acetylene flames. Oxygen is used commercially for the production of the oxy-hydrogen and oxy-coal gas flames, which are high temperature flames used for melting refractory metals such as platinum, for autogenous soldering, the production of the lime light (or "Drummond light"), etc. In these flames, a jet of hydrogen or coal gas is burnt at the mouth of a special blow-pipe, shown diagrammatically in Fig. 41, and oxygen is fed into the centre of the flame, thus producing a hot sharply-pointed blow-pipe flame. By directing the flame on to a cylinder of quicklime, a light of great luminosity, known as the lime light, is produced. Iron wire or steel watch spring may be readily burnt in the oxy-coal gas flame, the iron throwing out brilliant sparks and producing triferric tetroxide or magnetic oxide of iron (Fe_3O_4).

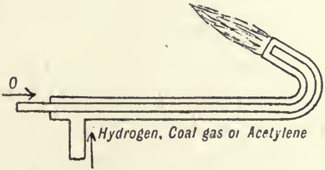


Fig. 41. Oxy-hydrogen flame.

$$3Fe+2O_2 \rightarrow Fe_3O_4$$

When the iron is burning, the supply of coal gas may be shut off and the metal will continue to burn in the jet of oxygen gas.

By feeding the coal gas flame with acetylene gas, an oxy-coal gas-acetylene flame is produced, which is intensely hot, and which is reducing in character. In oxy-acetylene welding, acetylene only is burnt and supplied with oxygen, such a flame being used for welding purposes and for cutting thick ingots and plates of steel.

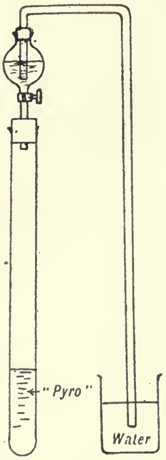


Fig. 42. Absorption of oxygen by pyrogallic acid solution.

Solubility of oxygen in alkaline pyrogallic acid solution. The alkaline pyrogallic acid solution is prepared by dissolving about 5 grams of pyrogallic acid in 100 c.c. of water and adding about 15 grams of caustic potash to the liquid. This liquid is then added gradually from a stoppered funnel to the pure oxygen gas in a long glass tube, Fig. 42, the entrance of the liquid being started by cooling the oxygen tube with a little ether. The "pyro" solution is shaken up to bring it into intimate contact with the oxygen, and finally, after adding the whole of the liquid, water may be admitted through the funnel as shown in the figure. If the oxygen gas is pure, the whole of the tube may be filled with liquid, showing the complete solubility of the oxygen. This method is used in gas analysis, for absorbing oxygen, and thus estimating its amount when mixed with other gases.

Oxides, oxidation and oxidising agents.

Oxides. Oxygen is one of the most active of the elements, and combines with all known non-metals and metals, with the exception of fluorine, producing compounds which have been already referred to as oxides. Most of these may be obtained by the direct combination of the elements with the oxygen.

The non-metallic oxides are, as a rule, acidic oxides, *i.e.*, they will produce acids by combination with water, whereas the greater number of the metallic oxides are termed basic oxides.

Oxidation and oxidising agents. The action of oxygen on non-metals and metals has been already dealt with, such action being known as oxidation. Thus, the action of oxygen gas on metallic copper (Fig. 13, p. 24), by means of which black copper oxide is obtained, may be looked upon as a typical oxidising action. Other examples of oxidation may be shown by dropping concentrated nitric acid slowly upon red-hot powdered charcoal in a porcelain dish, the carbon taking fire in the oxygen gas evolved by the nitric acid; or a piece of charcoal or sulphur may be dropped upon melted potassium chlorate or potassium nitrate in a test tube, the charcoal and sulphur taking fire and deflagrating violently on the melted compound. These actions are similar to the burning of carbon and sulphur in oxygen gas, the potassium chlorate or nitrate acting as the oxidising agent, and supplying the oxygen gas which combines chemically with the carbon or sulphur.

These actions are the basis of those which take place in the burning of gunpowder and modern high explosives, the gunpowder being a mixture of potassium nitrate, carbon and sulphur, though the actual actions which take place are somewhat complex; similarly, in modern high explosives, an oxidisable substance is mixed with a body which supplies oxygen and which acts as an oxidising agent.

The spontaneous combustion of greasy rags is also an example of oxidation, the oxygen of the air combining slowly with the oxidisable oil, producing heat, and ultimately this may accumulate to a sufficient extent to fire the greasy material.

Other elements besides oxygen may act as oxidising agents, thus, chlorine, bromine, etc., may act as powerful bodies for bringing about oxidation. Ferrous chloride, $FeCl_2$, *e.g.*, is oxidised to ferric chloride by means of chlorine, or the action may be brought about indirectly by heating a solution of ferrous chloride with hydrochloric acid and a substance which will evolve oxygen, such as nitric acid, potassium chlorate, etc. In this case, the oxygen oxidises the hydrogen of the hydrochloric acid, liberating chlorine which combines with the ferrous chloride, thus:

$$\underset{\substack{| \\ \text{ferrous chloride}}}{2FeCl_2} + 2HCl + \underset{\substack{| \\ \text{from} \\ \text{oxidising agent}}}{O} \rightarrow H_2O + \underset{\substack{| \\ \text{ferric chloride}}}{2FeCl_3}$$

A similar action takes place with a solution of ferrous sulphate, but in this case sulphuric acid is preferably used in conjunction with the oxidising agent, thus producing a solution of ferric sulphate:

$$\underset{\text{ferrous sulphate}}{2FeSO_4} + H_2SO_4 + O \rightarrow H_2O + \underset{\text{ferric sulphate}}{Fe_2(SO_4)_3}$$

An **oxidising agent** may therefore be defined as a substance which will give up oxygen, or an element or group of elements similar to oxygen, to another substance.

CHAPTER X

OXIDES, ACIDS, BASES AND SALTS

Classification of oxides: Acid oxides or anhydrides: Bases or basic oxides: Amphoteric oxides: Peroxides: Acids: Basicity of acids: Hydroxides and alkalis: Indicators: Normal, acid and basic salts: Reversible, balanced, and mass actions.

Classification of oxides.

The various oxides of the elements are classified into three main groups: (1) Acid oxides or anhydrides, (2) Bases or basic oxides, (3) Peroxides.

(1) **Acid oxides or anhydrides.** The name oxygen is derived from Greek words, meaning "acid producer," and was named from the fact that it was noticed early that it gave rise to oxides which produced acids. The oxygen theory of the production of acids, as stated by Lavoisier, was however later abandoned, as oxygen not only produces oxides which are not acidic, but it will be shown later that the essential constituent of an acid is hydrogen.

The non-metallic oxides are generally acidic in character, such oxides as carbon dioxide, sulphur dioxide and trioxide, phosphorus pentoxide, etc., giving rise to carbonic acid, sulphurous and sulphuric acids and phosphoric acid when dissolved in water, thus:

$$\underset{\text{carbonic anhydride}}{CO_2} + H_2O \rightarrow \underset{\text{carbonic acid}}{H_2CO_3}$$

$$\underset{\text{sulphurous anhydride}}{SO_2} + H_2O \rightarrow \underset{\text{sulphurous acid}}{H_2SO_3}$$

$$\underset{\text{sulphuric anhydride}}{SO_3} + H_2O \rightarrow \underset{\text{sulphuric acid}}{H_2SO_4}$$

$$\underset{\text{phosphoric anhydride}}{P_4O_{10}} + 6H_2O \rightarrow \underset{\text{phosphoric acid}}{4H_3PO_4}$$

The term anhydride means "without water," and the name carbonic anhydride may therefore be interpreted "carbonic acid without water"; such a method of naming the acid oxide is advantageous, as it indicates the particular acid which is formed from the oxide by combination with water.

A few of the metallic oxides are acidic in character, giving rise to acids when dissolved in water, *e.g.*, chromic anhydride or trioxide, CrO_3, manganic anhydride or trioxide, MnO_3, permanganic anhydride, Mn_2O_7:

$$\underset{\text{chromic anhydride}}{CrO_3} + H_2O \rightarrow \underset{\text{chromic acid}}{H_2CrO_4}$$

$$\underset{\text{manganic anhydride}}{MnO_3} + H_2O \rightarrow \underset{\text{manganic acid}}{H_2MnO_4}$$

$$\underset{\text{permanganic anhydride}}{Mn_2O_7} + H_2O \rightarrow \underset{\text{permanganic acid}}{H_2Mn_2O_8}$$

(2) **Bases or basic oxides.** Each metal gives rise to at least one basic oxide, and in some cases forms two such oxides, a basic oxide being one which will combine with an acid oxide with the production of a compound known as a salt. Examples of such oxides are: sodium oxide, Na_2O; potassium oxide, K_2O; calcium oxide or quicklime, CaO; barium monoxide, BaO; zinc oxide, ZnO; magnesium oxide or magnesia, MgO; aluminium oxide or alumina, Al_2O_3; lead monoxide or litharge, PbO; ferrous oxide, FeO; ferric oxide, Fe_2O_3; cuprous oxide, Cu_2O; cupric oxide, CuO; manganous oxide, MnO; manganic oxide, Mn_2O_3.

Amphoteric oxides. A few of the oxides, generally metallic, act both as basic and acidic oxides, zinc oxide, *e.g.*, is usually basic in character, giving rise to zinc compounds, such as zinc sulphate, by combination with an acid oxide:

$$ZnO + SO_3 \rightarrow ZnSO_4$$

It may, however, act as a weak acid, giving rise to zincates by combination with certain bases; the formation of sodium zincate has been already shown in the preparation of hydrogen in Chapter VIII, by the action of zinc on caustic soda, and this compound contains both the basic oxide, Na_2O, and the weak acidic oxide, ZnO.

$$\text{Sodium zincate} \rightarrow Na_2O, ZnO \text{ or } Na_2ZnO_2$$

(3) **Peroxides.** Certain elements, generally metals, form oxides which contain more oxygen than the basic oxides containing the same elements and these are known as peroxides; examples of these are manganese peroxide, MnO_2; barium peroxide, BaO_2; lead peroxide, PbO_2; hydrogen peroxide, H_2O_2.

They all evolve oxygen when heated, and the metallic peroxides also possess the following general properties:

(1) They evolve oxygen when heated with dilute sulphuric acid:

$$2MnO_2 + 2H_2SO_4 \rightarrow 2MnSO_4 + 2H_2O + O_2$$

(2) They evolve chlorine when heated with concentrated hydrochloric acid:

$$MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$$

Tetroxides. There are a few oxides known which are termed tetroxides, such as triferric tetroxide, Fe_3O_4; trimanganic tetroxide, Mn_3O_4; lead tetroxide, Pb_3O_4 (red lead). These oxides may be looked upon as double oxides, *e.g.*, Fe_3O_4 may be supposed to be a compound of ferrous and ferric oxides and is sometimes termed ferroso-ferric oxide, FeO, Fe_2O_3; similarly Mn_3O_4 is MnO, Mn_2O_3, and Pb_3O_4 is $PbO_2, 2PbO$. The constitutions of these oxides have been determined from their properties, for example, when red lead is treated with hot dilute nitric acid, the latter dissolves out lead monoxide from the red lead in the same manner that nitric acid dissolves pure lead monoxide, PbO, and at the same time leaves behind a residue of lead peroxide, PbO_2.

Acids.

As already described, certain acids may be produced by the combination of water with acid oxides, but, in addition, there are acids known which contain no oxygen, such as hydrochloric acid, HCl, hydrosulphuric acid, H_2S, etc. We may therefore classify the acids into two groups, *viz.*:

(1) Hydr-acids, which contain no oxygen, such as those just mentioned;

(2) Oxy-acids, containing oxygen, such as carbonic acid, H_2CO_3, sulphuric acid, H_2SO_4, phosphoric acid, H_3PO_4.

The essential element in an acid is hydrogen, and an acid may be defined as a compound containing hydrogen, which may be replaced by a metal when the latter is added to the acid in the form of an oxide or hydroxide. This action will be described shortly in dealing with the methods of producing salts.

Basicity of acids. The basicity of an acid is shown by the number of atoms of hydrogen in the molecule of the acid, which may be replaced by atoms of metals, *e.g.*, hydrochloric acid (HCl) is monobasic, sulphuric acid (H_2SO_4) is dibasic and phosphoric acid (H_3PO_4) is tribasic. It does not follow, however, that all the atoms of hydrogen in an acid may be replaced by a metal, as acetic acid, which is monobasic, has the formula $H_4C_2O_2$, the molecule containing four atoms of hydrogen though only one is capable of replacement by a metal, such as sodium. When the molecule contains more than one atom of replaceable hydrogen, the general term polybasic is often applied to the acid.

Hydroxides and alkalis.

All the basic oxides form compounds with water which are termed hydroxides. These are not as a rule formed by direct combination of the basic oxide with water, but generally have to be prepared by indirect methods. Sodium, potassium, and calcium oxides combine readily with water, forming hydroxides, thus:

$$Na_2O + H_2O \rightarrow 2NaOH$$
$$K_2O + H_2O \rightarrow 2KOH$$
$$CaO + H_2O \rightarrow Ca(OH)_2$$

The distinctive group of elements present in these compounds is the —OH group, known as the hydroxide group, though the compounds are in some cases written CaO, H_2O instead of $Ca(OH)_2$, the latter, however, being the preferable one.

When the hydroxide is soluble in water, the body possesses certain properties, known as **alkaline properties**, and the compound is termed an **alkali**; an alkali may therefore be briefly defined as a soluble hydroxide.

It should be noted that ammonia gas (NH_3) dissolves in water with the production of ammonium hydroxide, a fact which will be dealt with later in describing ammonium compounds.

$$NH_3 + H_2O \rightarrow NH_4OH$$

Ammonium hydroxide possesses alkaline properties, the ammonium group (NH_4) behaving as if it were a single atom of an alkali metal, such as sodium or potassium.

Such a group of atoms, acting apparently like the atom of an element, is sometimes termed a **compound radical.**

Acid and alkaline substances—Indicators.

The acids and alkalis possess as a rule certain properties, such as sourness in the case of acids, soapiness to the touch in the case of alkalis, which are, however, only incidental to these substances, and these bodies cannot accurately be defined by an enumeration of these properties. The acid and alkaline characters of these two classes of substances are usually best recognised by their effects upon certain bodies, frequently colouring matters, which are termed indicators. Thus, litmus, which is a vegetable colour derived from the litmus plant, is purplish in colour when dissolved in water, but is turned red by a small quantity of hydrochloric or sulphuric acid, and turned blue by a small quantity of sodium or potassium hydroxide. It should be noted, however, that other substances besides acids and alkalis may have an effect upon indicators, and the latter are only used to indicate acidity and alkalinity.

The indicators in common use are litmus, either in solution or as litmus paper, phenol phthalein dissolved in alcohol (0·1 gram in 100 c.c. of alcohol) and methyl orange (1 gram dissolved in 100 c.c. of a mixture of equal parts of alcohol and water). When an acid and an alkali are mixed in equivalent proportions, so that the resulting liquid shows neither acidity nor alkalinity, the solution is said to be neutral, and the process of production is termed neutralisation. The effects of acid and alkali upon the common indicators may be summarised as follows:

Indicator	Acid	Alkali	Neutral
Litmus	red	blue	purple
Phenol phthalein	colourless	violet	colourless
Methyl orange	pink	yellow	orange
Congo red	blue	terra-cotta red	terra-cotta red

Litmus is affected by carbonic acid in solution, whereas methyl orange is not, so that the latter is generally used for detecting a small quantity of mineral acid, such as hydrochloric or sulphuric acid in the presence of carbon dioxide in solution. Methyl orange cannot be used in the presence of organic acids. Congo red may be used as an indicator for mineral acids in the presence of organic acids. Phenol phthalein is one of the most sensitive indicators for alkalinity, but cannot be used in the presence of ammonia and under these conditions methyl orange should be used. Phenol phthalein is the most suitable indicator for organic acids.

Salts.

An acid may be neutralised as described above by an alkali or hydroxide, or a base, and a compound known as a salt is produced, the hydrogen of the acid being either partially or completely replaced by the metal of the hydroxide or base.

A salt is always formed when a base combines with an acid oxide, *e.g.*, quicklime combines with carbon dioxide producing calcium carbonate:

$$CaO + CO_2 \rightarrow CaCO_3$$

A typical method for the production of a salt may be shown by the gradual addition of a dilute solution of hydrochloric acid to a caustic soda (sodium hydroxide) solution, the acid being conveniently added from a burette. One or two drops of methyl orange solution are added to the alkali, and the addition of acid is continued until the liquid just turns orange in colour, when the addition of a further drop of acid will turn the liquid decidedly pink in colour. Under these conditions a neutral, or very slightly acid, solution of ordinary salt (sodium chloride) is formed, this substance being usually termed common salt to distinguish the body from this class of substances, known as salts, the following action having taken place:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

The solid salt may be obtained by boiling away the water of the solution.

The following are the typical methods of preparing the compounds known as salts:

(1) The combination of basic oxides with acid oxides or acids:

$$\underset{\text{base}}{CaO} + \underset{\text{acid oxide}}{CO_2} \rightarrow \underset{\text{salt}}{CaCO_3}$$

$$\underset{\text{base}}{ZnO} + \underset{\text{acid}}{H_2SO_4} \rightarrow \underset{\text{salt}}{ZnSO_4} + \underset{\text{water}}{H_2O}$$

(2) The combination of alkalis with acid oxides or acids:

$$\underset{\text{alkali}}{Ca(OH)_2} + \underset{\text{acid oxide}}{CO_2} \rightarrow \underset{\text{salt}}{CaCO_3} + \underset{\text{water}}{H_2O}$$

(This latter reaction is the one taking place when lime water is turned milky.)

$$\underset{\text{alkali}}{NaOH} + \underset{\text{acid}}{HCl} \rightarrow \underset{\text{salt}}{NaCl} + \underset{\text{water}}{H_2O}$$

It will be observed that in these processes, the action results only in the production of a salt or a salt and water, the metal of the base or hydroxide replacing the hydrogen of the acid.

Ammonium hydroxide (NH_4OH) behaves like the metallic hydroxides and forms a series of salts, which are known as ammonium salts, the following being typical actions :

$$NH_4OH + HCl \rightarrow \underset{\text{ammonium chloride}}{NH_4Cl} + H_2O$$

$$2NH_4OH + H_2SO_4 \rightarrow \underset{\text{ammonium sulphate}}{(NH_4)_2SO_4} + 2H_2O$$

(3) In addition, salts may frequently be obtained by the solution of a metal or a carbonate of a metal in a suitable acid ; examples of the former action have been already dealt with in the solution of zinc, magnesium, etc., in hydrochloric, sulphuric, and nitric acids, and of the latter action in Chapter VI, in the preparation of carbon dioxide. In this case, the marble (calcium carbonate), which is itself a salt, dissolves in the hydrochloric acid with the production of another salt (calcium chloride), which remains in solution, thus :

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

(4) A further method of preparing salts, in the case of those which are insoluble in water, is by the process of precipitation. In this case two soluble salts are mixed together, and if it is possible by the interchange of the metals to form a compound which is insoluble in water, a reaction will take place. Thus, sodium carbonate and calcium chloride are both soluble in water, but, if the sodium is replaced by calcium, insoluble calcium carbonate is formed, so that on mixing the two solutions the following reaction takes place :

$$\underbrace{\underset{\substack{\text{calcium}\\\text{chloride}}}{CaCl_2} + \underset{\substack{\text{sodium}\\\text{carbonate}}}{Na_2CO_3}}_{\text{both soluble}} \rightarrow \underset{\substack{\text{insoluble}\\\text{calcium}\\\text{carbonate}}}{CaCO_3} + \underset{\substack{\text{soluble}\\\text{sodium}\\\text{chloride}}}{2NaCl}$$

The insoluble calcium carbonate is thrown out from the solution as a solid, and will separate as a sediment or may be filtered off from the soluble sodium chloride.

This process, which is known as "**double decomposition**," is of the greatest importance in chemical work, and often accounts for the precipitation of insoluble substances in fibres when the conditions are suitable.

Each acid thus produces a series of compounds, which are salts, and these bodies are therefore not only very numerous but are amongst the most important of the compounds dealt with in inorganic chemistry.

Thus hydrochloric acid produces chlorides, sulphuric and nitric acids produce sulphates and nitrates and so on.

Classification of salts: normal, acid and basic salts. Salts are sometimes classified according to their action on certain indicators, thus sodium carbonate is alkaline to litmus, whereas copper sulphate and alum redden blue litmus, but these properties are more or less incidental to the compounds and the ordinary salts are as a rule neutral in character to indicators.

A better method of classification is according to the composition, the compounds being divided in this way into (1) normal, (2) acid, (3) basic salts.

Normal salts are compounds in which the whole of the hydrogen of the acid is replaced by a metal, such as magnesium sulphate ($MgSO_4$), or Epsom salts ($MgSO_4, 7H_2O$), sodium carbonate (Na_2CO_3), or washing soda ($Na_2CO_3, 10H_2O$).

Acid salts are produced from polybasic acids, and in these compounds only part of the hydrogen of the acid is replaced by a metal, and some of the acidic hydrogen still remains in the compounds, *e.g.*, $NaHCO_3$, sodium bicarbonate or bicarbonate of sodium; $NaHSO_4$, sodium bisulphate or bisulphate of sodium ("nitre cake"). These compounds are usually acidic in character to indicators, though not always, *e.g.*, sodium bicarbonate is neutral to methyl orange. The composition of these substances is frequently represented by formulae which show the presence of free acid in their molecules, as in Na_2SO_4, H_2SO_4 ($2NaHSO_4$), which is sometimes used for sodium bisulphate, and this explains why "nitre cake" is valuable as a substitute for sulphuric acid in many operations, *e.g.*, in the carbonising of wool, etc.

The term bi- is very commonly used to denote these compounds though other names are employed, *e.g.*, $NaHSO_4$ is named sodium bisulphate, or sodium hydrogen sulphate or acid sodium sulphate.

Basic salts. Many normal salts have the power of combining with a further quantity of base, and forming compounds termed basic salts; these are usually less soluble than the corresponding normal salts. Bismuth, antimony, tin and copper, are among the metals which readily form basic compounds, normal bismuth chloride and nitrate combining with a further quantity of base (Bi_2O_3) to form the basic bismuth chloride and nitrate. These are shown in the following formulae:

Normal bismuth chloride, $BiCl_3$; basic bismuth chloride, $BiCl_3, Bi_2O_3$;
Normal bismuth nitrate, $Bi(NO_3)_3$; basic bismuth nitrate, $Bi(NO_3)_3, Bi_2O_3$.

The formulae of these basic compounds may also be written $Bi_3O_3Cl_3$ and $Bi_3O_3(NO_3)_3$ or $BiOCl$ and $BiONO_3$, in which form they are named bismuth oxy-chloride and bismuth oxy-nitrate. The compounds, however, actually contain water of crystallisation, and a still further method of representing the formulae is sometimes therefore used, *viz.*:

$BiOCl, H_2O$ or $Bi(OH)_2Cl$, basic bismuth chloride;
$BiONO_3, H_2O$ or $Bi(OH)_2NO_3$, basic bismuth nitrate;

though these substances are frequently written in their simplest form, $BiOCl$ and $BiONO_3$.

The compounds are readily formed by the action of water on the normal salts, and frequently the water of crystallisation brings about a slow change to the basic condition, thus :

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$
$$Bi(NO_3)_3 + H_2O \rightleftharpoons BiONO_3 + 2HNO_3$$

This process, by which the compound is partly broken up by the action of water, is termed **hydrolysis.** The basic compounds are less soluble than the normal compounds, and are therefore often precipitated by the addition of water to a strong solution of the normal salt, though as the above actions are reversible, the addition of sufficient of the free acids, hydrochloric acid or nitric acid, will send the reaction towards the left and the normal salt is re-formed.

It frequently happens that a normal salt, which should be easily soluble in water, such as bismuth nitrate, is found to be partially insoluble. This is due, as stated above, to the basic salt having been formed to some extent by the action of water of crystallisation, and to obtain the substance in solution a small quantity of the free acid, in this case nitric acid, must be added, when the whole of the salt will pass into solution as the normal compound.

Balanced and mass actions.

The above actions have been stated to be reversible, that is, they may take place either towards the right or left of the equation according to the conditions, and are represented thus :

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

Under suitable conditions, all four substances, *viz.*, normal bismuth chloride, water, bismuth oxy-chloride, and hydrochloric acid, may be present, and the reaction is then termed a balanced action. Under these conditions, the action is continually going on in both directions ; the molecules of normal salt are being continually decomposed forming the basic salt, but just as many molecules of the normal salt are being re-formed from the basic salt in any given length of time.

This balance, however, may be disturbed in either direction, that is towards the formation of the basic salt or the normal salt, by varying the mass of one or other of the substances. Such a reaction is termed a "mass" action. By adding, *e.g.*, a further amount of water, further quantities of $BiOCl$ and HCl are formed, that is, the balance is disturbed towards the right of the equation, although a new point is arrived at where the reaction again becomes balanced with all four substances present. A similar result is attained by diminishing the mass of the hydrochloric acid in unit volume of the liquid.

On the other hand, by increasing the mass of the HCl, the reaction is sent towards the left of the equation.

By the addition, therefore, of a very large quantity of water, practically complete precipitation of the basic salt may be obtained, and similarly by the addition of a relatively large quantity of hydrochloric acid, the whole of the basic salt may be redissolved with formation of the normal compound, the effect of increasing infinitely the amount of one of the substances being to send the reaction completely towards the opposite side of the equation.

CHAPTER XI

NOMENCLATURE OF COMPOUNDS—VALENCY

NAMING OF OXIDES, ACIDS, BASES AND SALTS: -OUS AND -IC COMPOUNDS: PER-COMPOUNDS: VALENCY AND CONSTITUTION OF OXIDES, ACIDS, BASES AND SALTS.

Naming of compounds.

It has already been shown that certain metals form two basic oxides, *e.g.*, copper forms Cu_2O and CuO. In such cases the termination **-ous** is given to the lower oxide, *i.e.*, the one containing a lesser proportion of oxygen, and the termination **-ic** to the one containing the higher proportion, though in some cases the termination is added to a portion derived from the Latin name of the element. We therefore have the following names:

Cu_2O, cuprous oxide;	CuO, cupric oxide;
FeO, ferrous oxide;	Fe_2O_3, ferric oxide;
Hg_2O, mercurous oxide;	HgO, mercuric oxide.

This method is now always used in preference to the older method of prefixing the terms proto- and per- to the names, as in the cases of the iron oxides, which were at one time known as iron protoxide (FeO) and iron peroxide (Fe_2O_3). This method, although still in use, should be carefully avoided by the student, as in modern nomenclature the term per- has quite a different meaning, and a peroxide is not a basic oxide.

A similar method is used for naming acids and anhydrides, SO_2 and H_2SO_3 being sulphurous anhydride and acid, whilst SO_3 and H_2SO_4 are known as sulphuric anhydride and acid respectively.

There may, however, be several acids formed from the same elements, and in such cases the prefixes, hypo- and per-, are employed to denote the other acids as shown in the following examples, the acids with less oxygen than the -ous compound being termed the hypo- compound, whilst the acid with more oxygen than the -ic compound is named the per- acid.

Naming of acids.

Acid	Name	Acid	Name
HNO	Hyponitrous acid	$HClO_3$	Chloric acid
HNO_2	Nitrous acid	$HClO_4$	Perchloric acid
HNO_3	Nitric acid	H_3PO_2	Hypophosphorous acid
$HClO$	Hypochlorous acid	H_3PO_3	Phosphorous acid
$HClO_2$	Chlorous acid	H_3PO_4	Phosphoric acid

These terms **-ous** and **-ic** are also employed in naming salts obtained from -ous and -ic basic oxides, thus -ous oxides give rise to -ous salts and -ic oxides to -ic salts. Ferrous chloride and sulphate are obtained from ferrous oxide, and ferric chloride and sulphate from ferric oxide:

$$\underset{\text{ferrous oxide}}{FeO} + H_2SO_4 \rightarrow \underset{\text{ferrous sulphate}}{FeSO_4} + H_2O$$

$$\underset{\text{ferric oxide}}{Fe_2O_3} + 6HCl \rightarrow \underset{\text{ferric chloride}}{2FeCl_3} + 3H_2O$$

The terms protochloride, protosulphate, perchloride and persulphate, etc., for these compounds should also be avoided; they are now rarely used, and are never employed in the official publications of societies, such as the *Journal of the Chemical Society.*

The acidic portion of the salt is named according to the acid from which the salt is obtained, thus a hydr-acid gives rise to a salt ending in **-ide**, an -ous acid forms an **-ite** salt and an -ic acid an **-ate** salt; these methods may be summarised:

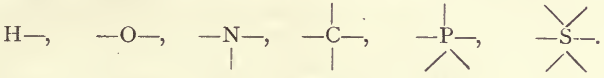
Acids	**Salts ending in**
Hydr-	-ide
Hypo- ous	Hypo- ite
-ous	-ite
-ic	-ate
Per- ic	Per- ate

Thus hydrochloric (HCl), hydrobromic (HBr), and hydrosulphuric acids (H_2S) give rise to hydrochlorides, hydrobromides, hydrosulphides, though these are commonly named, chlorides, bromides and sulphides; hypochlorous acid forms hypochlorites, sulphurous acid forms bisulphites and sulphites, sulphuric acid forms bisulphates and sulphates, and persulphuric acid (HSO_4) forms persulphates.

Valency and constitution of compounds.

The term valency is derived from the word "equivalency," and is used for denoting the number of atoms of hydrogen which are equivalent to one atom of the element or group of elements in a compound; the valency therefore shows the number of atoms of hydrogen which one atom of the element will combine with, or will replace, in forming a compound. When one atom of the element will combine with or will replace one atom of H, the element is termed a monad or is said to be monovalent ; when one atom replaces or combines with two atoms of H, the element is a diad or is divalent ; three atoms of H, a triad ; four atoms, a tetrad ; five atoms, a pentad ; and six atoms, a hexad.

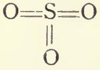
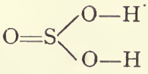
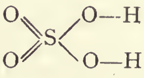
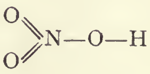
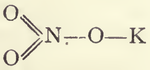
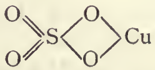
These facts may be represented symbolically :



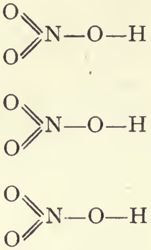
monad	diad	triad	tetrad	pentad	hexad
hydrogen	oxygen	nitrogen	carbon	phosphorus	sulphur

The valency of some of the atoms may vary, frequently in pairs of valencies, thus sulphur may be in certain cases a diad, in others a tetrad, and even a hexad, but sufficient may be known of the valencies of the elements to enable us to build up the structure of the compounds graphically and gain in some cases a knowledge of the properties of the substance. This is of far greater importance amongst the compounds of carbon, and in such cases we have to deal with fewer elements, in which the valencies remain, as a rule, constant.

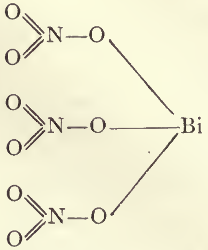
These graphic, structural or constitutional formulae are represented thus :

water, H_2O	$H—O—H$
sulphur dioxide, SO_2	$O{=}S{=}O$
sulphur trioxide, SO_3	 $\begin{matrix} O{=}S{=}O \\ \Vert \\ O \end{matrix}$
sulphurous acid, H_2SO_3	
sulphuric acid, H_2SO_4	
nitric acid, HNO_3	
potassium nitrate, KNO_3	
copper sulphate, $CuSO_4$	

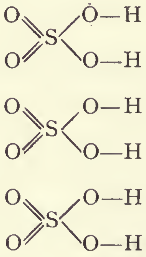
More complex formulae of salts are built up from the graphic formulae of the acids, and the valencies of the metals replacing the hydrogen of the acids, thus, the formulae of bismuth nitrate and sulphate are obtained by first writing down the structural formulae of the nitric and sulphuric acids, and then replacing the hydrogen in the acids by bismuth which is a triad; three molecules of the acid must be used in each case and one atom of bismuth introduced in the case of the nitrate and two atoms in the case of the sulphate, thus:



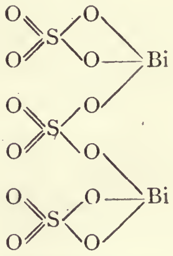
3 molecules of nitric acid



1 molecule of bismuth nitrate



3 molecules of sulphuric acid



1 molecule of bismuth sulphate

In the case of oxy-acids, the basicity of the acid is shown by the number of —OH groups in the structural formulae, and, to indicate these, the formulae of such oxy-acids as nitric acid (HNO_3), sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4), etc., are frequently written in an abbreviated form, thus $NO_2(OH)$, $SO_2(OH)_2$ and $PO(OH)_3$.

Owing to the variable valency of some of the elements, we cannot write the structural formulae of inorganic compounds at all times with certainty, but a table of valency may be used for the metallic and acidic parts of acids, hydroxides, basic oxides, and salts, which is of great value in arriving at the correct formulae of the various compounds.

Valency of acid and salt radicals. We have already seen that water may be split up into hydrogen and oxygen by a current of electricity, H, which is electro-positive, being liberated at the negative electrode, whilst O which is electro-negative is liberated at the positive electrode. Similarly, most acids and salts are broken up by a current of electricity into H or the metal, which is electro-positive, and the acidic portion of the compound, such as $—NO_3$, $—SO_4$, which is electro-negative. As we shall see later in dealing with the electrolysis of compounds, these groups of elements, which are known as radicals, may not be able to exist in the free state, and secondary or further reactions may take place. The H, the metals and these radicals in acids, hydroxides, basic oxides and salts have, however, a definite valency, and if these are arranged in tabular form under electro-positive and electro-negative columns, for both monads, diads, triads, and tetrads, we may obtain a scheme from which the formulae of acids, basic oxides, hydroxides, and normal salts may be written in a reliable manner, by combining together electro-positive and electro-negative radicals according to their respective valencies. These facts are summarised in the tabular statement below :

Table of valency of salt radicals.

Monads				Diads			
Electro-positive (+)		Electro-negative (−)		Electro-positive (+)		Electro-negative (−)	
H—	Hydrogen	—OH	Hydroxide	Zn=	Zinc	=O	Oxide
Na—	Sodium	—Cl	Chloride	Mg=	Magnesium	=SO_3	Sulphite
K—	Potassium	—Br	Bromide	Ca=	Calcium	=SO_4	Sulphate
NH_4—	Ammonium	—I	Iodide	Ba=	Barium	=S	Sulphide
Ag—	Silver	—F	Fluoride	Sr=	Strontium	=CO_3	Carbonate
		—NO_3	Nitrate	Pb=	Lead	=C_2O_4	Oxalate
		—NO_2	Nitrite	Mn=	Manganous	=CrO_4	Chromate
		—ClO	Hypochlorite	Ni=	Nickelous	=SiO_3	Silicate (meta-)
		—ClO_3	Chlorate	Co=	Cobaltous		
				Cd=	Cadmium		
				Hg(ic)=	Mercuric		
				Hg_2(ous)=	Mercurous		
				Fe(ous)=	Ferrous		
				Cu(ic)=	Cupric		
				Cu_2(ous)=	Cuprous		
				Sn(ous)=	Stannous		

Triads				Tetrads			
Electro-positive (+)		Electro-negative (−)		Electro-positive (+)		Electro-negative (−)	
Bi≡	Bismuth	≡PO_4	Phosphate	Sn(ic)≣	Stannic	≣SiO_4	Silicate (ortho-)
Sb≡	Antimonious	≡PO_3	Phosphite	Pt(ic)≣	Platinic		
As≡	Arsenious	≡AsO_4	Arseniate				
Au≡	Auric	≡AsO_3	Arsenite				
Cr(ic)≡	Chromic						
Fe(ic)≡	Ferric						
Al≡	Aluminium						

The above list is not, of course, exhaustive, but, as the student becomes accustomed to its use, he will be able to add to it. It may be noted that in some cases both the -ous and -ic compounds of the same metal are given, these being, in both cases, common compounds, whereas in other cases the -ous, *e.g.*, nickelous, or the -ic, *e.g.*, auric, compounds only are given as these are the only common compounds of these metals.

It may also be noted that in the case of mercurous and cuprous compounds, two atoms of the metal are considered to be the diad radical; the single atom in each case may of course be looked upon as a monad, but the formulae usually given to the common -ous compounds of these metals will be arrived at by taking the two atoms as a diad radical.

To obtain formulae from these radicals, electro-positive must be combined with electro-negative in equivalent proportions, according to the respective valencies as follows: 1 monad with 1 monad; 1 diad with 1 diad; 1 triad with 1 triad; 1 tetrad with 1 tetrad; 1 diad with 2 monads; 1 triad with 3 monads; 1 tetrad with 4 monads; 1 tetrad with 2 diads, or with 1 triad and 1 monad; 2 triads with 3 diads (equal in each case to 6 monads); 3 tetrads with 4 triads and so on.

The formulae for acids may be obtained by combining the electro-negative radicals (with the exception of —O and —OH) with H, *e.g.*, HCl, HBr, HI, H_2S, H_2SO_4, H_3AsO_4 (arsenic acid), H_3AsO_3 (arsenious acid), H_4SiO_4 (silicic acid). The formulae of the basic oxides are obtained by combining the metals with oxygen, and the hydroxides by combination with —OH, thus, K_2O, ZnO, Bi_2O_3, SnO_2, KOH, $Cu(OH)_2$ (cupric), $Bi(OH)_3$, $Sn(OH)_4$ (stannic hydroxide). The formulae of salts are obtained by combining the metals with acidic radicals; thus, AgCl, silver chloride; $ZnCl_2$, zinc chloride; $AuCl_3$, auric chloride (commonly called gold chloride); $SnCl_4$, stannic chloride; $CuCl_2$, cupric chloride; Cu_2Cl_2, cuprous chloride; $ZnSO_4$, zinc sulphate; $Bi_2(CO_3)_3$, bismuth carbonate, and so on. In some cases, the valency is shown by attaching dashes, or Roman numerals, to the radicals, thus, ferric oxide, $Fe_2^{III}O_3^{II}$; bismuth sulphate, $Bi_2^{III}(SO_4)_3^{II}$.

The table may also be used for writing the formulae of some compounds containing more than one electro-positive radical, thus ammonium magnesium phosphate is $NH_4^{I}Mg^{II}PO_4^{III}$, sodium hydrogen sulphate is $Na^{I}H^{I}SO_4^{II}$. In such cases the valencies of the electro-positive radicals must be balanced against the electro-negative ones. This may not always be possible, unless the actual name is taken into consideration, *e.g.*, sodium hydrogen phosphate does not sufficiently describe a compound, as this may be written Na_2HPO_4 or NaH_2PO_4; both these compounds may be obtained, but are known as disodium hydrogen phosphate (or hydrogen disodium phosphate) and sodium dihydrogen phosphate.

CHAPTER XII

ACIDIMETRY AND ALKALIMETRY

NORMAL AND STANDARD SOLUTIONS: APPARATUS USED IN VOLUMETRIC ANALYSIS: PREPARATION OF NORMAL ACID AND ALKALI: VALUATION OF SODA ASH, WASHING SODA AND AMMONIA: ESTIMATION OF CARBONATE AND HYDROXIDE IN CAUSTIC ALKALI AND CARBONATES: VALUATION OF ACIDS: ANALYSES OF AMMONIUM SALTS.

Acidimetry and alkalimetry. These terms are employed to denote the processes in use for the estimation of acids and alkalis in bodies, either gaseous, liquid or solid, and this forms an important branch of volumetric analysis. For this purpose, it is necessary to know the proportions in which the various acids and alkalis combine together, which can be determined from the equations showing the chemical actions, thus:

$$\underset{\underbrace{23+16+1}_{40}}{\mathrm{NaOH}} + \underset{\underbrace{1+35\cdot5}_{36\cdot5}}{\mathrm{HCl}} \rightarrow \mathrm{NaCl}+\mathrm{H_2O}$$

It follows, from the above equation, that 40 parts by weight of sodium hydroxide will combine exactly with 36·5 parts by weight of hydrochloric acid, and if we know the amount of one of these bodies in a solution, we may determine the amount of the other in a solution of unknown strength, by making use of one solution to exactly neutralise the other.

Standard and normal solutions. The preparation of solutions of acid and alkali of a definite and known strength is therefore of the greatest importance, and great care must be bestowed on the preparation of an accurate standard. Solutions of known strength are termed standard solutions, though it is more convenient to prepare the solution so that it bears some definite relationship to the molecular weight of the substance in solution.

A convenient starting point for the preparation of such a solution is one containing hydrochloric acid, which is made of such a strength that there is present in 1000 c.c. of the liquid an amount of the acid which contains 1 part by weight (1 gram) of acidic H.

The molecular weight of HCl, *viz.*, 36·5 grams, contains 1 gram of hydrogen, and the solution is therefore prepared with 36·5 grams by weight of HCl gas in 1000 c.c. of the liquid, such a solution of hydrochloric acid being known as a **normal solution** of the acid and labelled N/1 HCl. Solutions may be made of twice, one-half, one-fifth, one-tenth, or even one-hundredth of this strength, and are then termed 2N, N/2, N/5, N/10, or N/100 HCl, and each of these may be employed in analysis under suitable conditions.

From the equation given above, it follows that, as 40 grams of NaOH combine with 36·5 grams of HCl, 40 grams of solid NaOH per litre of liquid will be contained in N/1 NaOH.

By making use of the equations below, we may obtain the amounts of $NaHCO_3$, Na_2CO_3, H_2SO_4, etc., which are contained in the N/1 solutions, respectively, of these substances:

$$\underset{\underbrace{23+1+12+48}_{84}}{NaHCO_3} + \underset{\underbrace{1+35{\cdot}5}_{36{\cdot}5}}{HCl} \rightarrow NaCl+CO_2+H_2O$$

$$\underset{\underbrace{46+12+48}_{106}}{Na_2CO_3} + \underset{2(\underbrace{1+35{\cdot}5}_{73})}{2HCl} \rightarrow 2NaCl+CO_2+H_2O$$

$$\underset{2(\underbrace{23+16+1}_{80})}{2NaOH} + \underset{\underbrace{2+32+64}_{98}}{H_2SO_4} \rightarrow Na_2SO_4+2H_2O$$

$$\underset{\underbrace{46+12+48}_{106}}{Na_2CO_3} + \underset{\underbrace{2+32+64}_{98}}{H_2SO_4} \rightarrow Na_2SO_4+CO_2+H_2O$$

From these, and other similar reactions, we obtain the strengths for the normal solutions of various acids and alkalis:

	Acid or Alkali	**Strength of N/1 solution in grams per litre of liquid**
Acids	Hydrochloric acid (HCl)	36·5 grms.
	Sulphuric acid (H_2SO_4)	49 „
	Nitric acid (HNO_3)	63 „
	Acetic acid ($H_4C_2O_2$)	60 „
Alkalis	Sodium bicarbonate ($NaHCO_3$)	84 grms.
	Sodium carbonate (Na_2CO_3)	53 „
	Potassium carbonate (K_2CO_3)	69 „
	Sodium hydroxide (NaOH)	40 „
	Potassium hydroxide (KOH)	56 „
	Ammonia (NH_3)	17 „

It should be noted that it is the acidic hydrogen which regulates the number of grams of the acid in the normal solution. Thus acetic acid, $H_4C_2O_2$ contains only 1 atom of replaceable H, or is monobasic (see Chapter XXVI), and the molecular weight of acetic acid is therefore contained in 1 litre of N/1 acetic acid.

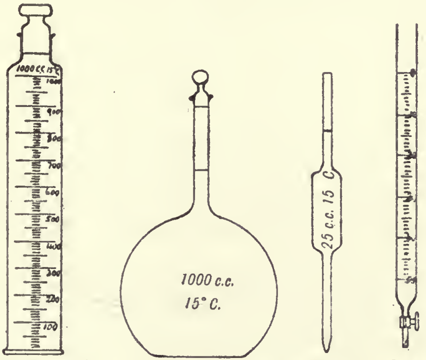
It follows from the above description that 1 litre of N/1 acid will exactly neutralise 1 litre of a N/1 alkali, and from the figures given, we may obtain the following results:

1 c.c. of N/1 acid (HCl, H_2SO_4 or HNO_3) = 0·084 gram of $NaHCO_3$
= 0·053 gram of Na_2CO_3 = 0·040 gram of $NaOH$
= 0·056 gram of KOH = 0·017 gram of NH_3, etc.

The strengths of other solutions, such as 2N or N/10, may be similarly expressed, thus N/10 acid = 0·0053 gram of Na_2CO_3, etc.

By preparing N/1 solutions of acid or alkali, we may therefore use these by the process of neutralisation to find the strengths of unknown solutions of alkali or acid, or for valuing specimens of acid, or alkali, such as soda ash (commercial Na_2CO_3), washing soda (Na_2CO_3, $10H_2O$), caustic alkalis, etc.

Apparatus used in acidimetry and alkalimetry. The apparatus used is simple in character, and consists mainly of graduated vessels for either making up solutions to a definite volume, or for measuring out aliquot portions of the liquid, and are shown in Fig. 43.



Graduated Cylinder *Graduated Litre Flask* *Pipette* *Burette*

Fig. 43. Graduated vessels for volumetric analysis.

The **graduated flasks** are made commonly of 1 litre (1000 c.c.), or ¼ litre (250 c.c.), or 1/10 litre (100 c.c.) in capacity, the vessels *containing* (not delivering) these amounts of liquid at 15° C. if filled up accurately to a mark made on the neck of the flask.

The **pipette** is made to *deliver* a definite volume of liquid, generally 100 c.c., 50 c.c., 25 c.c., 10 c.c., or 5 c.c., when first filled with liquid to a mark on the stem, and then drained for about 30 seconds after the main portion of the liquid has run out, by touching the point of the pipette against the surface of the receiving vessel. The pipette is filled by suction with the mouth to a point a little above the mark, the finger placed quickly and tightly on the top, and gently released to allow the meniscus of the liquid to come accurately to the mark; the definite volume of the liquid may then be delivered into a suitable vessel.

The **burette** is a graduated stoppered tube, generally made to deliver 50 c.c. of liquid, and graduated usually in 1/10ths of a c.c. It is supported in a suitable stand known as a burette stand, or an ordinary iron stand and clamp may be used, though, in the latter case, care must be taken that it is clean and that there is no possibility of dust falling into the liquid under treatment.

Graduated cylinders. 1000 c.c., 500 c.c., 250 c.c., and 100 c.c. cylinders are also commonly employed for diluting measured bulks of liquid to a given amount.

Process of neutralisation used in acidimetry and alkalimetry. The method is carried out as already described in Chapter X, for the production of a salt from acid and alkali, the experiment being preferably performed in a porcelain dish, or in a conical flask of suitable size standing on a white tile or a sheet of white paper, so that the change in colour of the indicator may be readily observed.

Indicators. The indicators in common use are litmus, methyl orange and phenol phthalein in the form of solutions, one or two drops only of the indicator being employed; in the case of methyl orange, it will be found that a very small quantity of the liquid will give a sharper indication of the change of colour, than if a larger quantity is employed.

The **litmus solution** is prepared by digesting powdered litmus (about 10 grams) with about 100 c.c. of water, the liquid being then divided into two equal parts; one portion is turned just blue with a few drops of NaOH solution, the other portion being just reddened with HCl, and the two portions are then mixed, thus producing a neutral litmus solution, purple in colour.

Methyl orange solution is prepared by dissolving 0·1 gram of methyl orange in 100 c.c. of a mixture of equal parts of alcohol and water.

Phenol phthalein solution is prepared by dissolving 1 gram of phenol phthalein in 100 c.c. of alcohol.

Preparation of a N/1 solution of sodium bicarbonate. The standardisation of a N/1 acid solution is usually recommended from a standard solution of sodium carbonate, the latter solid being prepared by the ignition of solid sodium bicarbonate. This process, however, always results in the formation of a certain amount of caustic soda, even up to 1 per cent. in amount, both the following actions taking place:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O,$$
$$NaHCO_3 \rightarrow NaOH + CO_2.$$

A much more accurate standard is obtained by the preparation first of all of purified bicarbonate, but this is a somewhat long and tedious process, and a sufficiently accurate standard may be obtained by employing the solid pure bicarbonate as sold and dissolving this in water.

21 grams of pure sodium bicarbonate are weighed off accurately on a large watch glass, and transferred to a 250 c.c. flask. This is best done by putting a short-stemmed funnel into the neck of the flask, and washing the weighed solid through into the flask by a continuous stream of distilled water from a wash bottle. After thoroughly rinsing the watch glass and funnel, the flask is filled to the mark with distilled water, and the solution well shaken till the whole of the solid is dissolved.

Preparation of N/1 hydrochloric or sulphuric acid. About 110 c.c. of concentrated hydrochloric acid (sp. gr. 1·2) are poured into about 500 c.c. of distilled water, and the liquid made up to 1 litre in bulk with distilled water. In the case of N/1 H_2SO_4, about 30 c.c. of concentrated sulphuric acid (sp. gr. 1·84) are poured carefully into distilled water, the liquid cooled and then made up to 1 litre. The liquid in each case will be approximately normal in strength, and its exact strength may be found by means of N/1 $NaHCO_3$.

For this purpose 25 c.c. of the N/1 $NaHCO_3$ are measured out by means of the pipette into a conical flask, one drop of methyl orange added, and the acid is added gradually from the burette until the liquid just turns orange in tint. The reading of the burette is then taken, and one more drop of the acid afterwards added to ascertain that its addition produces a full pink tint in the liquid.

Two such titrations are made and the mean of the two results taken as the correct amount:

25 c.c. of the N/1 $NaHCO_3$ require 24·6 c.c. of acid.

∴ 24·6 c.c. of the acid = 25 c.c. of the N/1 acid, or 24·6 c.c. of the acid require the addition of 0·4 c.c. of water to produce N/1 acid.

950 c.c. of the acid would require $\frac{0·4 \times 950}{24·6} = 15·5$ c.c. of water.

950 c.c. of the acid are therefore measured out accurately by means of a graduated cylinder, and mixed with 15·5 c.c. of distilled water measured from a burette; the result should be an accurate N/1 acid, but to ensure that this is the case, it should be again titrated against 25 c.c. of the N/1 $NaHCO_3$. 25 c.c. of the N/1 $NaHCO_3$ should require 25 c.c. of the N/1 acid.

Instead of making the acid exactly normal, the so-called "factor" of the acid may be found thus:

$$\begin{aligned} 24·6 \text{ c.c. of the acid} &= 25 \text{ c.c. of a N/1 acid.} \\ 1 \text{ c.c. ,, ,, ,,} &= \frac{25}{24·6} \text{ ,, ,, ,,} \\ &= 1·016 \text{ ,, ,, ,,} \end{aligned}$$

Factor = 1·016.

The acid is then labelled N/1 acid, factor 1·016.

This means that 1 c.c. of the acid contains as much actual acid as 1·016 c.c. of N/1 acid, and whatever number of c.c.'s of acid are used in any titration or analysis must be multiplied by the factor 1·016, and this will give the equivalent number of cubic centimetres of normal acid.

Preparation of N/1 sodium hydroxide. About 45 grams of stick caustic soda are dissolved in water, cooled, and made up to 1 litre in bulk with distilled water. 25 c.c. of N/1 acid are measured out, and the caustic soda run into the acid from a burette, using phenol phthalein as indicator until a permanent purple tint is obtained in the liquid after shaking.

A calculation, similar to the one for the N/1 acid, may then be made to ascertain the amount of water which must be added to a definite bulk of the caustic soda, in order to make the liquid exactly normal; or the factor may be calculated thus:

24·5 c.c. of caustic soda required for 25 c.c. N/1 acid, factor 1·016.

∴ 24·5 c.c. of caustic soda solution = 25 × 1·016 c.c. N/1 acid or N/1 NaOH.

= 25·4 c.c. ,, ,, ,, ,,

$$1 \text{ c.c. of caustic soda solution} = \frac{25{\cdot}4}{24{\cdot}5} \text{ c.c. N/1 NaOH}$$

$$= 1{\cdot}04.$$

∴ solution = N/1 NaOH, Factor 1·04.

Estimation of alkali in a specimen of "soda ash" or "pure alkali" (commercial dry sodium carbonate). 5 grams of soda ash are accurately weighed out, dissolved in water and made up to 100 c.c. with distilled water in a graduated flask. 25 c.c. of the liquid are titrated with N/1 acid using methyl orange as indicator. The weights and results should always be entered up in a notebook at the time they are made, and the calculation may then be made as follows:

5 grams of soda ash taken. Dissolved in water and made up to 100 c.c.

(1) 25 c.c. of this solution required 23·1 c.c. N/1 acid, Factor 1·016.

(2) 25 c.c. of this solution required 23·2 c.c. N/1 acid, Factor 1·016.

Mean result = 23·15 c.c.

23·15 c.c. N/1 acid, Factor 1·016 = 23·15 × 1·016 c.c. N/1 acid

= 23·52 c.c. N/1 acid.

1 c.c. of N/1 acid = 0·053 gram Na_2CO_3.

23·52 c.c. of N/1 acid = 0·053 × 23·52 grams Na_2CO_3

= 1·246 grams Na_2CO_3.

∴ 25 c.c. of the soda ash solution contain 1·246 grams Na_2CO_3.

100 c.c. ,, ,, ,, ,, 4 × 1·246 grams Na_2CO_3

= 4·984 grams Na_2CO_3.

∴ 5 grams of soda ash contain 4·984 grams Na_2CO_3.

100 „ „ „ $\frac{4{\cdot}984 \times 100}{5}$ grams Na_2CO_3

$= 99{\cdot}7$ per cent. Na_2CO_3.

Instead of calculating the amount of Na_2CO_3 in the sample, the amount of the basic oxide (Na_2O) may be calculated, by employing the value = 1 c.c. of N/1 acid = 0·031 gram Na_2O.

The theoretical percentage of Na_2O in pure dry Na_2CO_3 may be obtained thus:

$$\underset{\underbrace{46+12+48}_{106}}{Na_2CO_3} \text{ contains } \underset{\underbrace{46+16}_{62}}{Na_2O} + CO_2.$$

106 parts by weight of Na_2CO_3 contain 62 parts by weight of Na_2O.

100 parts by weight of Na_2CO_3 contain $\frac{62 \times 100}{106} = 58{\cdot}5$ per cent. Na_2O.

"**Pure alkali**" is often guaranteed and sold as 58 per cent. Na_2O purity, or commercially it is sometimes named 58° purity.

Estimation of alkali in washing soda, potassium carbonate, caustic soda, caustic potash, etc. The amount of Na_2CO_3 in washing soda ($Na_2CO_3, 10H_2O$) is estimated in a similar manner, but about 15 grams of the washing soda should be accurately weighed out and dissolved in water, making up to 100 c.c. About 7 grams should be accurately weighed out in the case of potassium carbonate, about 4 grams in the case of NaOH and 6 grams in the case of KOH, and the weighed quantity is in each case dissolved in water and made up to 100 c.c. The titration is carried out in a similar manner with each substance, but in calculating the percentage of substance, the following values will be employed:

with K_2CO_3 : 1 c.c. N/1 acid = 0·069 gram K_2CO_3.
with NaOH : 1 c.c. N/1 acid = 0·040 gram NaOH.
with KOH : 1 c.c. N/1 acid = 0·056 gram KOH.
with $Na_2CO_3, 10H_2O$: 1 c.c. N/1 acid = 0·143 gram $Na_2CO_3, 10H_2O$
or 0·053 gram Na_2CO_3.

Estimation of ammonia (NH_3) in a sample of strong ammonia liquor. A concentrated solution of ammonia in water, or ammonium hydroxide, NH_4OH, is continually becoming weaker by loss of NH_3 gas when exposed to the air, and the solution should therefore be weighed off in a stoppered bottle, termed a weighing bottle, the solution being preferably mixed with water. About 10 c.c. of water are placed in a weighing bottle, and the whole accurately weighed; about 5 c.c. of the concentrated ammonia solution are added and a further weighing made, the difference in the two weights being the quantity of ammonia liquor taken for analysis. The whole of the liquid is transferred to a 100 c.c. graduated flask, the bottle rinsed and the rinsings added to the liquid in the flask; finally the liquid is made up to the 100 c.c. mark with distilled water. The titration is made as before; 1 c.c. of N/1 acid=0·017 gram of ammonia (NH_3).

Estimation of sodium carbonate and caustic soda in commercial soda ash or commercial caustic soda. Commercial specimens of soda ash often contain both carbonate and caustic alkali; and specimens of caustic generally contain some carbonate, through absorption of CO_2 by exposure to air. If the caustic alkali is valued according to the amount of NaOH it contains, it becomes of importance to estimate the amount of alkali which it contains as carbonate. About 5 grams of the substance are weighed out accurately, dissolved and made up with distilled water to 100 c.c.

25 c.c. of this liquid are measured out into a large porcelain dish, 3 or 4 drops of phenol phthalein are added, and the liquid titrated by running acid slowly but continuously into the alkaline solution. The tip of the burette should be put below the liquid during the titration, and the liquid kept well stirred until the colour of the phenol phthalein just disappears. It is of importance that no carbon dioxide must escape from the liquid during this portion of the titration, the sodium carbonate being converted into sodium bicarbonate, which is neutral to phenol phthalein, and at the same time the caustic soda is completely neutralised, the following reactions taking place:

$$NaOH + HCl \rightarrow NaCl + H_2O$$
$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

A drop of methyl orange is then added, the tip of the burette withdrawn from the liquid, and the titration continued until the liquid turns orange in tint, the following action taking place:

$$NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$$

From these reactions it will be seen that the whole of the caustic soda is neutralised in the first part of the titration, using phenol phthalein, but, for the complete neutralisation of one molecule of sodium carbonate, two molecules of acid are necessary, one molecule being added during the titration with phenol phthalein and one in the latter portion of the titration with methyl orange.

The number of c.c.'s required with methyl orange represents half the carbonate, and by doubling this amount the carbonate can be calculated. The number of c.c.'s required with phenol phthalein represents half the carbonate plus the whole of the caustic, so that from the difference between the number of c.c.'s required with phenol phthalein and the methyl orange, the caustic may be calculated.

Example:

5 grams of soda ash taken and made up to 100 c.c. with distilled water.

25 c.c. titrated.

$$\text{Mean of two results : } \begin{cases} \text{with phenol phthalein } 12\cdot5 \text{ c.c. } N/1 \text{ acid.} \\ \text{with methyl orange } 11\cdot0 \text{ c.c. } N/1 \text{ acid.} \end{cases}$$

1·5 c.c. of N/1 HCl required to neutralise NaOH.

22 c.c. " " " Na_2CO_3.

1 c.c. of N/1 HCl = 0·040 gram of NaOH.

∴ 5 grams of soda ash contain 0·04 × 1·5 × 4 gram NaOH and per cent. of

$$NaOH = \frac{0\cdot04 \times 1\cdot5 \times 4 \times 100}{5} = 4\cdot8 \text{ per cent. } NaOH.$$

1 c.c. of N/1 HCl = 0·053 gram Na_2CO_3.

∴ 5 grams of soda ash contain 0·053 × 22 × 4 grams Na_2CO_3 and per cent. of $Na_2CO_3 = \frac{0\cdot053 \times 22 \times 4 \times 100}{5} = 93\cdot3$ per cent. Na_2CO_3.

$$\text{Results of analysis} = \begin{cases} Na_2CO_3 = 93\cdot3 \text{ per cent.} \\ NaOH \ = \ 4\cdot8 \text{ per cent.} \\ \text{Moisture or other salt impurities} = 1\cdot9 \text{ per cent.} \end{cases}$$

Estimation of strengths of acids, e.g., hydrochloric, sulphuric, acetic, formic or oxalic acids. A weighed quantity of the acid is taken, and made up to 100 c.c. with distilled water. 25 c.c. of the liquid are titrated with N/1 NaOH, using phenol phthalein as indicator, until a drop of the alkali gives a permanent purple coloration. The following weights are convenient amounts to take with moderately pure acids: HCl—12 to 15 grams; H_2SO_4—5 grams; oxalic acid ($H_2C_2O_4$, $2H_2O$)—6 grams; acetic acid ($H_4C_2O_2$)—6 grams; formic acid (H_2CO_2)—4 to 5 grams. The following values are taken for the strength of the N/1 NaOH solution: 1 c.c. of N/1 NaOH = 0·0365 gram HCl = 0·049 gram H_2SO_4 = 0·063 gram $H_2C_2O_4$, $2H_2O$ = 0·045 gram $H_2C_2O_4$ = 0·060 gram $H_4C_2O_2$ = 0·046 gram H_2CO_2.

These figures are of course obtained from the reactions taking place, which are shown in the following equations:

$$\underbrace{NaOH}_{40} + \underbrace{HCl}_{36\cdot5} \rightarrow NaCl + H_2O$$

$$\underbrace{2NaOH}_{\underbrace{2 \times 40}_{80}} + \underbrace{H_2SO_4}_{98} \rightarrow Na_2SO_4 + 2H_2O$$

$$\underbrace{H_2C_2O_4,\ 2H_2O}_{\underbrace{90 + (2 \times 18)}_{126}} + \underbrace{2NaOH}_{\underbrace{2 \times 40}_{80}} \rightarrow \underset{\substack{\text{sodium} \\ \text{oxalate}}}{Na_2C_2O_4} + 4H_2O$$

$$\underbrace{H_4C_2O_2}_{60}+\underbrace{NaOH}_{40}\rightarrow \underset{\text{sodium acetate}}{NaH_3C_2O_2+H_2O}$$

$$\underbrace{H_2CO_2}_{46}+\underbrace{NaOH}_{40}\rightarrow \underset{\text{sodium formate}}{NaHCO_2+H_2O}$$

It will be noted from the above equations, that oxalic acid is a dibasic acid, whilst acetic and formic acids are monobasic, but these facts will be dealt with more in detail later when the organic acids are described.

Estimation of ammonia in ammonium salts. When an ammonium salt, such as ammonium chloride, is heated with caustic alkali, it is decomposed according to the following equation:

$$\underset{\underbrace{14+4+35\cdot5}_{53\cdot5}}{NH_4Cl}+\underset{40}{NaOH}\rightarrow NaCl+NH_3+H_2O$$

By boiling a known weight of an ammonium compound with a measured quantity of N/1 NaOH solution in excess until the whole of the ammonia gas has been displaced, the reaction above will be complete; the excess of N/1 NaOH remaining in the liquid may then be titrated by means of a N/1 HCl solution, and the amount of N/1 NaOH which has been consumed by the ammonium salt may be deduced. It is, however, essential that an excess of alkali should be used, which may be indicated by mixing a drop of the solution on a white tile with phenol phthalein, after the boiling is finished. The whole of the ammonia gas must be boiled off, which may be ensured by boiling for 5 or 10 minutes after the odour of ammonia is no longer perceptible in the evolved steam.

The method is known as "backward titration," and such methods are often employed in volumetric analysis.

Example:

5 grams of commercial ammonium chloride taken and made up to 100 c.c.

25 c.c. of this solution mixed with 50 c.c. of N/1 NaOH and boiled till free of ammonia gas.

Titrated with N/1 HCl—26·8 c.c. N/1 HCl required.

26·8 c.c. N/1 HCl = 26·8 c.c. N/1 NaOH.

∴ 50 c.c. − 26·8 c.c. = 23·2 c.c. N/1 NaOH have combined with the NH_4Cl.

1 c.c. of N/1 NaOH = 0·0535 gram NH_4Cl.

∴ 23·2 „ „ = 0·0535 × 23·2 „

∴ 5 grams of commercial NH_4Cl contain 0·0535 × 23·2 × 4 grams of NH_4Cl, and per cent. of NH_4Cl in salt $= \dfrac{0\cdot0535 \times 23\cdot2 \times 4 \times 100}{5}$,

$= 99\cdot3$ per cent. NH_4Cl.

CHAPTER XIII

FURTHER STUDY OF WATER

NATURAL FORMS OF WATER: HARDNESS OF WATER: SUITABILITY FOR STEAM RAISING AND SCOURING PURPOSES: DETERMINATION OF PERMANENT AND TEMPORARY HARDNESS: METHODS OF SOFTENING HARD WATER: WATER FOR DRINKING PURPOSES: DALTON AND HENRY'S LAW OF SOLUBILITY OF GASES.

Natural forms of water.

The following table gives the approximate average composition of the chief types of natural waters, the amounts of the dissolved solids being expressed in grains per gallon, and the gases in cubic centimetres per litre.

	Rain water	Spring water	Mineral water (Bath)	River water (Thames)	Sea water
Solids	2·4	14	165	20·5	2450
Gases	21	25·5	35	53	35

Rain water. The amount of impurity in rain water is very small, but varies within fairly considerable limits according to the atmospheric conditions and place of collection. For example, rain water collected in country districts contains some of the atmospheric gases in solution, but is otherwise generally free from dissolved solid matter. When collected in a large town it may, in addition, contain sulphur gases, derived from the burning of coal, and may further be polluted with soot, solid matter in solution, and suspended dust, substances which are generally present in the atmosphere.

Spring water. Spring waters, as a rule, contain dissolved solid matter, although a few springs are known which give practically pure water, and the nature of the dissolved substance will vary according to the character of the strata through which the water has percolated.

The substances most commonly found in solution in spring waters are calcium and magnesium bicarbonates, sulphates and chlorides, and these bodies, as will be described later, give rise to the property known as "hardness" of water. In addition to these substances, there may be others present in such amount, that they give special characteristics to the spring water. Thus, a water very rich in calcium bicarbonate is known as a calcareous spring (*e.g.*, the petrifying springs of Matlock and Knaresborough); one containing bicarbonate of iron is known as a chalybeate spring (*e.g.*, Tunbridge Wells); siliceous springs contain silica (*e.g.*, the geysers of Iceland); and sulphur springs contain soluble sulphides and sulphuretted hydrogen gas (*e.g.*, Harrogate waters).

Mineral waters. Some spring waters are particularly rich in dissolved solid matter, and are termed mineral waters, as, for example, those of Bath, Harrogate, etc. In some cases a predominant substance may give a particular character to the water, such as the magnesia waters of Harrogate and Epsom, which contain large quantities of magnesium sulphate, and the Glauber-salt water of Marienbad, which contains sodium sulphate.

River water. River water contains as a general rule more dissolved solid and gaseous matter than the natural forms already dealt with, and, in addition to the substances mentioned under spring water, it may contain a considerable quantity of decaying vegetable and animal substance, known as organic matter, both in solution and in suspension.

The amount of dissolved solid matter, however, varies considerably in rivers in different districts, depending upon the character of the earth's crust through or over which the water has passed. Thus, the River Dee in Scotland, passing through a granitic district, takes up little dissolved matter, whereas in a limestone or chalk district, a river may contain a moderately large quantity of calcium carbonate. The Thames, as a river, may be considered to be a fairly average example, and it has been estimated that it carries past Kingston nearly 2,000 tons of solid matter per day, either in solution or suspension, and of this amount 1,000 tons is carbonate of lime (chalk or limestone), in solution as a bicarbonate.

Sea water. Sea water is the most impure form of natural water, especially with regard to the number of substances found in it, and it has been stated that all the known elements are present in sea water.

The chief substances in solution in sea water are sodium chloride (salt), magnesium chloride, magnesium sulphate, calcium sulphate, potassium chloride, magnesium bromide, etc., the total amount of solid matter being approximately $3\frac{1}{2}$ per cent., and about three-fourths of this solid matter is ordinary salt.

Hardness of water.

As already mentioned, the substances, which are most common in natural waters, are calcium and magnesium compounds, generally bicarbonates, sulphates and chlorides; the presence of these substances prevents the water lathering immediately with a soap, and the water is said to be "hard." These salts readily combine with soap, which is also a salt, a double decomposition taking place, and the sodium or potassium present in the hard or soft soap is replaced by the calcium or magnesium forming a calcium or magnesium soap. These are sticky, curdy, insoluble substances, which remain in suspension in the water, and if the water is being used for scouring purposes these soaps are very objectionable, as they become entangled in the fibres and are afterwards difficult to remove. There is further a great loss in soap, as the latter is of no value for scouring purposes until the whole of the lime or magnesia compounds in solution in the water have been entirely decomposed. Water, however, which is soft, or which is free from calcium or magnesium compounds, such as distilled or rain water, produces an immediate lather with soap, without the formation of the objectionable lime or magnesia soaps.

Temporary and permanent hardness. The hardness of water is of two kinds, temporary and permanent, the former being easily removed by boiling the water, whilst the permanent hardness is not removed in this way.

Temporary hardness is due to the presence of calcium or magnesium bicarbonates in solution, whilst permanent hardness is due to the presence of sulphates or chlorides of calcium or magnesium.

It has already been mentioned that carbon dioxide turns lime water milky, and this may be shown by passing a stream of carbon dioxide gas through a solution of lime water, a sediment of insoluble calcium carbonate being produced, thus:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

If the stream of carbon dioxide is continued, the calcium carbonate gradually dissolves forming an unstable, but more soluble, compound, known as calcium bicarbonate, thus:

$$CaCO_3 + CO_2 + H_2O \rightarrow \underset{\text{calcium bicarbonate}}{Ca(HCO_3)_2 \text{ or } CaCO_3, H_2CO_3}$$

Magnesium carbonate, which is also insoluble in water, may be similarly dissolved by carbonic acid forming magnesium bicarbonate, $Mg(HCO_3)_2$.

Rain water usually contains carbon dioxide in solution as carbonic acid, the gas having been derived from the atmosphere, or in the case of river water it is, in addition, derived from the decay of organic matter, and such water slowly attacks limestone, chalk, and rocks of similar composition, with the formation of calcium bicarbonate, and in some cases magnesium bicarbonate. The water is thus rendered temporarily hard.

The bicarbonates, however, are unstable bodies and are readily decomposed on heating, carbon dioxide being split off and carbonates of calcium or magnesium precipitated as a sediment, thus:

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$$

Consequently, waters which are temporarily hard are softened by boiling the water, the calcium and magnesium carbonates being precipitated.

Gypsum, $CaSO_4, 2H_2O$, is another mineral which is a common constituent of rocks, thick layers of this substance being commonly associated with strata containing rock salt, together with other calcium and magnesium compounds. As calcium sulphate is sparingly soluble in water, and as magnesium sulphate, calcium and magnesium chlorides are easily soluble bodies, water in passing through strata which contain these substances will take up some of these soluble salts. These bodies are not precipitated by boiling the water, until the solution is saturated with the solids, and consequently under normal conditions the hardness is not removed by boiling and the water is said to be permanently hard.

Production of boiler scale in using hard water for steam raising. In using hard water for steam raising, a sediment is continually being thrown out, consisting principally of calcium carbonate, generally with some magnesium carbonate and calcium sulphate. This sediment crystallises on the internal surface of the boiler giving rise to a hard crust, which is known as "boiler scale." The "furring" of pipes and kettles is due to the same process. Where hard water is used, the scale accumulates to such an extent, becoming in some cases an inch or more in thickness in the course of a few weeks, that it is necessary from time to time to cleanse the boiler by breaking and "chipping" the scale away from the internal parts. Such a process, frequently repeated, must damage and weaken the boiler plates in parts, in addition to attacking the metal in places; further, the presence of scale will result in a loss of fuel, and, with a water containing 20 grains of calcium carbonate per gallon (and some waters are much harder than this), this loss may amount on an average to as much as 25 per cent. of the fuel consumed.

Loss of soap in using hard water for scouring operations. As already mentioned, the calcium and magnesium compounds in solution in a hard water will combine with soap, and this may result in a very considerable loss. It has been estimated that 1000 gallons of a water, containing 20 grains of calcium carbonate per gallon, will decompose about 13 lb. of soap before the production of a lather for scouring purposes can begin, and even with a water which contains only 4 or 5 grains of

$CaCO_3$ per gallon, there will be a loss of about 3 lb. of soap for every 1000 gallons of water employed.

As there are textile factories that consume as much, or even more, than 150,000 gallons of water per day in the scouring of wool, it is obvious that the loss in soap may be very considerable, and any process which will diminish this loss is bound to be advantageous, especially as there is the additional advantage that the formation of large quantities of the objectionable lime and magnesium soaps is avoided.

Before, however, a water can be softened by the ordinary processes employed, it is necessary to determine the hardness, both temporary and permanent, of the water.

Determination of the hardness of water. There are two principal methods for the determination of hardness, *viz.*, Clarke's Soap Test and Hehner's Acid Test, and both these methods involve the determination of temporary and permanent hardness.

Standard solution of soap. The standard solution of soap is prepared by dissolving about 10 grams of best olive oil soap in a mixture of equal parts of alcohol and water. The solution of soap is then standardised against a standard solution of a lime compound, and the strength usually adjusted so that 1 c.c. of the liquid combines exactly with 1 milligram of calcium carbonate.

Preparation of the standard lime solution. 0·2 gram of Iceland spar (pure $CaCO_3$) is dissolved in dilute hydrochloric acid, and the solution evaporated carefully down to dryness in a porcelain dish, preferably by supporting the dish on a beaker of boiling water (a water bath) so as to avoid loss by spurting. When quite dry, the residue is dissolved in distilled water and then made up to 1 litre in bulk. As 1000 c.c. of the liquid contain 0·2 gram of $CaCO_3$, 50 c.c. of the liquid will contain 10 milligrams = 0·01 gram of $CaCO_3$. This bulk of liquid is taken for the standardisation.

Standardisation of the soap solution. 50 c.c. of the lime solution are measured out into a clean dry bottle of about 150 to 200 c.c. capacity, and the liquid mixed with 20 c.c. of water. This solution then contains 10 milligrams of $CaCO_3$ in 70 c.c. of liquid, or in 70,000 milligrams of water. As there are 70,000 grains in 1 gallon, this bulk of 70 c.c. may be looked upon as a "miniature gallon," in which the grain is represented by the milligram.

70 c.c. = 70 grams = 70,000 milligrams of water containing 10 milligrams of $CaCO_3$.

Replacing the term milligram by grain, we maintain the same proportion, and therefore

70,000 milligrams of water containing 10 milligrams of $CaCO_3$ represent 70,000 grains or 1 gallon of water containing 10 grains of $CaCO_3$.

It will be found that 1 c.c. of the soap solution is required to give a permanent lather with 70 c.c. of pure water, and if the soap solution is adjusted in strength so that 11 c.c. are required to give a permanent lather with the 70 c.c. of liquid measured out in the bottle, the soap solution will be of such a strength that 1 c.c. = 1 milligram of $CaCO_3$ or = 1 grain of $CaCO_3$ per gallon of water when 70 c.c. are taken for analysis.

To find the exact strength of the soap solution, the latter is added from a burette, 1 c.c. at a time, to the 70 c.c. of liquid in the bottle, and the liquid is shaken vigorously after each addition. This is continued until a lather is permanent on the surface of the liquid, when the bottle is left lying undisturbed on its side for 5 minutes. In all estimations of hardness, this method of finding the end point is adopted, but towards the end of the titration the soap solution may be added in smaller quantities, say 0·2 c.c. at a time.

Having found the number of c.c.'s required to produce a permanent lather with the liquid, a calculation is made of the amount of alcohol and water to be added to the soap solution to bring it to the correct strength, thus:

70 c.c. of liquid used = 10 grains of $CaCO_3$ per gallon.

9·5 c.c. of soap solution actually used in the titration.

9·5 c.c. of soap solution must be mixed with 1·5 c.c. of alcohol and water = 11 c.c.

950 c.c. of soap solution must be mixed with 150 c.c. of alcohol and water.

950 c.c. of the soap solution are measured out in a measuring cylinder, and 150 c.c. of a mixture of alcohol and water are added; this solution will then be of the required strength, that is, 1 c.c. of the liquid = 1 grain of $CaCO_3$ per gallon, when 70 c.c. are taken.

In all estimations of hardness, the result is expressed in terms of $CaCO_3$, whether the hardness is due to lime or magnesia compounds, sulphates, or chlorides, etc.

Estimation of total hardness of a water. 70 c.c. (a "miniature gallon") of the water are measured out into the stoppered bottle, and the soap solution added until a lather permanent for 5 minutes is obtained, the process being carried out exactly as in the standardisation of the soap solution. 1 c.c. is deducted from the number of c.c.'s required, and the number of c.c.'s remaining represents the number of grains per gallon of total hardness in the water, expressed as $CaCO_3$.

Example: 70 c.c. of water used.
12·5 c.c. of soap solution required.
Total hardness = 12·5 − 1 = 11·5 grains per gallon.

Determination of permanent hardness. 70 c.c. of the water are boiled down to about 20 c.c. in bulk, and the temporary hardness is thus removed from the liquid, which is then filtered. The clear liquid is made up to

70 c.c. in bulk with distilled water, and the hardness determined by the soap solution.

70 c.c. of water used.
4·5 c.c. of soap solution required.
Permanent hardness = 3·5 grains per gallon.
Temporary hardness = Total hardness − Permanent hardness
= 11·5 − 3·5 = 8 grains per gallon.

Notes on the determination of hardness by soap solution. The estimation is not reliable if 70 c.c. of the water require more than about 14 c.c. of the soap solution, and with such a hard water, 250 c.c. of the water should be made up to 500 c.c., or if necessary to a litre with distilled water, and the hardness of the diluted hard water determined. The final result must then be multiplied by 2 or 4, according to the amount of dilution.

The presence of magnesium compounds in the water gives rise to magnesia soaps, which form, however, somewhat slowly, and the estimation must therefore not be hurried, as in such cases a lather may be obtained which appears to be permanent, but on again shaking the lather may disappear. This is due to the magnesium compound only slowly decomposing the soap, so that on shaking a second time, the free soap in the liquid has disappeared. Further, the magnesium soap floating on the surface of the liquid imitates very closely a lather, but experience soon enables one to distinguish between a false lather, such as this, and a true lather.

The hardness is sometimes expressed in parts per 100,000 of water instead of in grains per gallon, and also in degrees of hardness, 1° H. representing 1 grain per gallon.

Waters containing 4 or 5 grains or less per gallon of water, total hardness, may be classed as soft waters, 5 to 20 grains per gallon as hard waters, and above 20 grains per gallon as being very hard.

Hehner's acid test for hardness. A deci-normal solution (N/10) of HCl is required, and this may be prepared by accurately measuring off 100 c.c. of N/1 HCl into a litre flask, and making up to the mark with distilled water.

1 c.c. of N/10 HCl = 0·005 gram of $CaCO_3$ = 5 milligrams of $CaCO_3$.

Determination of temporary hardness. 500 c.c. of the water are measured off into a porcelain dish, one drop of methyl orange added, and the liquid is titrated with the N/10 HCl until a pink colour is obtained. The bicarbonates of calcium and magnesium are decomposed by the HCl according to the following equations :

$$CaCO_3,\ H_2CO_3 + 2HCl \rightarrow CaCl_2 + 2CO_2 + 2H_2O$$
$$MgCO_3,\ H_2CO_3 + 2HCl \rightarrow MgCl_2 + 2CO_2 + 2H_2O$$

The number of c.c.'s required multiplied by five will give the number of milligrams of $CaCO_3$ present in 500 c.c. of the water, and the number in

70 c.c. may then be calculated. This will equal the number of grains of $CaCO_3$ per gallon.

500 c.c. of water taken.
11·43 c.c. of N/10 HCl used.
1 c.c. = 5 milligrams of $CaCO_3$.
∴ 11·43 c.c. = 11·43 × 5 = 57·15 milligrams of $CaCO_3$.
500 c.c. of water contain 57·15 milligrams of $CaCO_3$.

$$70\text{ c.c.} \quad ,, \quad ,, \quad \frac{57·15 \times 70}{500} \quad ,, \quad ,,$$

= 8 grains per gallon temp. hardness.

Determination of permanent hardness. For this estimation a decinormal solution of Na_2CO_3 (N/10) is required, and is prepared similarly to the N/10 HCl by diluting 100 c.c. of N/1 Na_2CO_3 to 1 litre with distilled water.

250 c.c. of the water to be tested are measured off, mixed with 25 c.c. of N/10 Na_2CO_3, and the liquid is evaporated to dryness. This removes both the temporary and permanent hardness, thus :

By boiling, temporary hardness is removed :

$$CaH_2(CO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$$

By the action of N/10 Na_2CO_3 on the permanent hardness, the lime and magnesium salts are precipitated, thus :

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$$

The residue is extracted with a small quantity of distilled water and filtered, the vessel and paper washed with a small quantity of distilled water, and the filtrate and washings are titrated with N/10 HCl to estimate the excess of N/10 Na_2CO_3 present. The number of c.c.'s of acid required will give the number of c.c.'s of N/10 Na_2CO_3 left in excess after removal of permanent hardness, and this amount subtracted from 25 c.c. (the no. of c.c.'s of N/10 Na_2CO_3 employed) will give the amount of N/10 Na_2CO_3 used up in precipitating the permanent hardness.

1 c.c. of N/10 Na_2CO_3 = 5 milligrams $CaCO_3$ as permanent hardness.
∴ No. of c.c.'s N/10 Na_2CO_3 used up × 5 = No. of milligrams of $CaCO_3$ in 250 c.c. of the water.

The number in 70 c.c. may then be calculated and gives the number of grains per gallon permanent hardness.

Example: 250 c.c. of water taken.
25 c.c. of N/10 Na_2CO_3 added.
22·5 c.c. of N/10 HCl required.

∴ 25 − 22·5 = 2·5 c.c. of N/10 Na_2CO_3 combined with permanent hardness.
1 c.c. of N/10 Na_2CO_3 = 5 mgs. of $CaCO_3$ as permanent hardness.
2·5 c.c. ,, = 12·5 ,, ,, ,,
∴ 250 c.c. of water contain 12·5 milligrams of $CaCO_3$.
∴ 70 c.c. ,, ,, 3·5 ,, ,,
= 3·5 grains per gallon permanent hardness.

Removal of hardness from water (softening of water). Clarke's process. There are various ways of removing the hardness from water. The temporary hardness may be almost entirely removed by boiling, or the whole of the hardness may be removed by soap, but neither of these methods lends itself for obvious reasons to commercial use.

Various compositions are sold for removing the hardness, or for preventing boiler scale, some of these being applied to the water externally and some in the boilers themselves, *e.g.*, mixtures containing calcium or sodium hydroxide and sodium carbonate ; or sodium meta-aluminate $NaAlO_2$ (Na_2O, Al_2O_3), the latter acting thus :

$$2NaAlO_2 + CaH_2(CO_3)_2 + 2H_2O \rightarrow CaCO_3 + Na_2CO_3 + 2Al(OH)_3$$

The method, which lends itself best to commercial application, known as Clarke's process, is the addition of slaked lime, $Ca(OH)_2$, for removal of temporary hardness, and of Na_2CO_3 for removal of permanent hardness, the latter substance in laundry operations being used in the form of washing soda for the same purpose.

It may seem curious at first sight to add lime for the removal of lime, but an inspection of the equation below will give at once the reason, the calcium hydroxide combining with the carbonic acid present in the calcium or magnesium bicarbonates and precipitating calcium carbonate, thus :

$$\begin{array}{r}\text{Temporary}\\ \text{hardness}\end{array}\left\{\begin{array}{l} Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O \\ Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow CaCO_3 + MgCO_3 + 2H_2O \end{array}\right.$$

The permanent hardness is removed thus :

$$\begin{array}{r}\text{Permanent}\\ \text{hardness}\end{array}\left\{\begin{array}{l} CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4, \\ MgCl_2 + Na_2CO_3 \rightarrow MgCO_3 + 2NaCl. \end{array}\right.$$

Calculation of the amounts of lime and soda ash (sodium carbonate) required for softening a hard water. The amounts of softening materials required for a given hardness may be calculated from the reactions above, the calculation being made in all cases for an amount of $CaCO_3$, as hardness, which is equivalent to the substance shown in the reaction :

$$\underset{\substack{\text{or}\\ CaCO_3,\ H_2CO_3\\ \underbrace{40+12+48}_{100}}}{Ca(HCO_3)_2} + \underset{\underbrace{40+16}_{56}}{CaO,\ H_2O} \rightarrow 2CaCO_3 + 2H_2O$$

The equation shows that 100 parts by weight of $CaCO_3$ as temporary hardness require 56 parts by weight of quicklime for its complete removal. The calculation for 1000 gallons of water containing 12·5 grains per gallon is made as follows:

1 gallon contains 12·5 grains of $CaCO_3$ as temporary hardness.
1000 gallons contain 12,500 " " " "
100 grains of $CaCO_3$ require 56 grains of quicklime.
12,500 " " " $\frac{56 \times 12,500}{100}$ grains of quicklime
$= 7000$ grains $= 1$ lb. of CaO.

The permanent hardness is removed by the addition of Na_2CO_3. Although the hardness may be due to say $MgSO_4$, the calculation is made from an equivalent quantity of $CaCO_3$, as the hardness is expressed in terms of $CaCO_3$; 1 molecule of $CaCO_3$ is equivalent to 1 molecule of $MgSO_4$ and the calculation is made as follows:

$$MgSO_4 + \underset{\underbrace{46+12+48}_{106}}{Na_2CO_3} \rightarrow MgCO_3 + Na_2SO_4$$

$$\underset{\underbrace{40+12+48}_{100}}{CaCO_3}$$

1 gallon of water contains 6·6 grains per gallon, $CaCO_3$, perm. hard.
1000 gallons " contain 6600 " " " "
100 grains of $CaCO_3$ (perm. hard.) require 106 grains Na_2CO_3.
6600 " " " " $\frac{106 \times 6600}{100}$ "
$= 6996$ grains
$=$ approx. 1 lb. of Na_2CO_3.

1000 gallons of a water, containing 12·5 grains per gallon, as temporary hardness, and 6·6 grains per gallon, permanent hardness, therefore require for the removal of the hardness 1 lb. of quicklime and approximately 1 lb. of soda ash or "pure alkali" (Na_2CO_3).

Even with the best conditions, however, the hardness cannot be entirely removed owing to the slight solubility of calcium carbonate, etc., and the result is considered good practice if the hardness is reduced to 2 or 3 grains per gallon. With magnesium compounds, however, even this result cannot be obtained, owing to the greater solubility of magnesium carbonate, which is formed in Clarke's process. In this case, it is found advantageous to add more calcium hydroxide to convert the magnesium carbonate into the less soluble calcium carbonate and magnesium hydroxide, thus:

$$MgCO_3 + Ca(OH)_2 \rightarrow \underbrace{CaCO_3 + Mg(OH)_2}_{\text{both less soluble than } MgCO_3}$$

If the amount of magnesium per gallon is known, the extra amount of lime required may be calculated, but as the estimation of magnesium is a long and tedious process, the amount of calcium hydroxide required is best found experimentally.

Experimental determination of amount of lime required for softening water. Lime factor. A standard solution of calcium hydroxide (N/10) is prepared and carefully standardised against N/10 HCl. 210 c.c. of water are measured off into a 250 c.c. graduated cylinder and 25 c.c. of N/10 calcium hydroxide are added, the liquid being well shaken at intervals during 2 hours, and the precipitate is allowed to settle. An aliquot portion of the clear liquid is then drawn off, say 70 c.c., and titrated by N/10 HCl, first using phenol phthalein as indicator till neutral, and then methyl orange till neutral. The liquid, before titration, will contain excess of calcium hydroxide, and a little calcium carbonate in solution. By deducting the number of c.c.'s of acid required when using the methyl orange as indicator from the number required when using the phenol phthalein, the amount of N/10 acid required to neutralise the calcium hydroxide is obtained, thus giving the amount of N/10 $Ca(OH)_2$ in excess. The amount which has combined with the hardness (temporary and magnesium hardness) may be deduced thus :

210 c.c. of water taken.
25 c.c. of N/10 calcium hydroxide added.

Total bulk of liquid = 235 c.c.

70 c.c. of the clear liquid titrated and required
3·45 c.c. of N/10 HCl with phenol phthalein,
0·05 c.c. „ „ „ methyl orange.

Therefore to neutralise the $Ca(OH)_2$,

70 c.c. of liquid require 3·4 c.c. of N/10 HCl,

$$235 \text{ c.c. } ,, \quad ,, \quad \frac{3{\cdot}4 \times 235}{70} = 11{\cdot}4 \text{ c.c. N/10 HCl}$$
$$= 11{\cdot}4 \text{ c.c. N/10 } Ca(OH)_2.$$

$\therefore$ 210 c.c. of water have consumed $25 - 11{\cdot}4$ c.c. N/10 $Ca(OH)_2$
$= 13{\cdot}6$ c.c. N/10 $Ca(OH)_2$.

Molecular weight of $Ca(OH)_2 = 74$ and $CaO = 56$.

N/1 $Ca(OH)_2 = 37$ grams of $Ca(OH)_2$ or 28 grams CaO per litre.

$\therefore$ 1 c.c. of N/10 $Ca(OH)_2 = 0{\cdot}0028$ gram CaO.
13·6 c.c. „ „ $= 0{\cdot}0028 \times 13{\cdot}6 = 0{\cdot}0381$ gram CaO.
210 grams of water require 0·0381 gram CaO.

$$70{,}000 \text{ grains (or 1 gallon) of water require } \frac{0{\cdot}0381 \times 70{,}000}{210} \text{ grains CaO.}$$

$$1000 \text{ gallons of water require } \frac{0{\cdot}0381 \times 70{,}000 \times 1000}{210 \times 7000} \text{ lb. CaO}$$
$$= 1{\cdot}81 \text{ lb. CaO (quicklime).}$$

The amount of soda ash required to remove the permanent hardness is found by calculation as previously described, and this is added to form magnesium carbonate which is then converted into the hydroxide by the $Ca(OH)_2$.

Softening trial. A trial may with advantage be made of the softening of a specimen of the water from the results obtained in the lime factor and the permanent hardness. Thus, 210 c.c. of the above water may be mixed with 13·6 c.c. of N/10 $Ca(OH)_2$ and the number of c.c.'s of N/10 Na_2CO_3 required for the permanent hardness as shown by Hehner's method. The water is shaken up during a period of 2 hours, settled, and the hardness of the clear liquid is determined by Hehner's or Clarke's method. If the total hardness is reduced to 2 or 3 grains per gallon, the softening may be considered satisfactory and the calculation is made for the bulk.

Softening of water. The slaked lime only dissolves sparingly in water, and is usually mixed up with water to form a milky liquid known as milk of lime. The milk of lime and the soda ash in solution are added as required to the water, frequently in open tanks, and any waste steam may be blown into the liquid to aid the precipitation of the calcium and magnesium compounds, which separate better in a granular form under these conditions. After settling, the clear softened water may be drawn off.

Various forms of apparatus are also made for the continuous softening of water, the reagents, milk of lime and soda ash solution, being run into the water continuously, in a quantity regulated automatically by a suitable apparatus, according to the amount required for a definite volume of water passing through the apparatus. The sediment is also separated off in the apparatus, so that a continuous supply of softened water is obtained.

"Permutit" process for softening water. During recent years a new process has been devised for the softening of water, which removes the hardness completely. The actual softening process is very simple, the water being simply filtered through a layer, a few feet in thickness, of a substance, termed "permutit," a trade name for a complex insoluble silicate of aluminium and sodium of the following composition, $Na_2O, Al_2O_3, 2SiO_2, 6H_2O$. This substance is similar in composition to certain naturally-occurring bodies, termed "zeolites," which also possess the property of decomposing lime and magnesia compounds in solution in water.

The formula of the compound may be represented, $Na_2\overline{P}$, and the reaction between the calcium or magnesium compounds and the permutit is represented, thus:

$$Na_2\overline{P} + CaSO_4 \rightarrow Ca\overline{P} + Na_2SO_4$$

$$\text{or } Na_2\overline{P} + MgCl_2 \rightarrow Mg\overline{P} + 2NaCl$$

Several different compounds, known as permutits, have been prepared, such as calcium permutit, magnesium permutit, stannous permutit, manganous permutit, etc. The manganous permutit is said to possess the property of removing small quantities of iron from solution, and also acts as a germicide to bacteria in water. The stannous permutit removes small quantities of gold from solution.

In the reaction above with lime or magnesium compounds, the permutit ultimately becomes sluggish in its action, but, as the second reaction shown above is reversible, and acts as a mass action, the permutit may be revivified by washing it with a strong brine solution. This re-forms the sodium permutit, the calcium and magnesium being removed in the excess of brine as calcium and magnesium chlorides, thus:

$$Ca\overline{P} + 2NaCl \rightleftharpoons Na_2\overline{P} + CaCl_2$$

The substance is therefore extremely valuable as a softening material, especially as the hardness is completely removed, though with very hard waters the permutit appears to become clogged in its action. The substance is also expensive, and the harder the water the greater the thickness of material which must be used. It would therefore appear that the material will find its most useful application in softening moderately hard water for scouring purposes in the textile industries, Clarke's method of softening by lime and soda being first used to reduce the hardness to 2 or 3 grains per gallon, and the last trace of hardness is removed by the permutit process. As already shown, this will result in a very considerable saving in soap for scouring purposes, and although the material is expensive, the cost is soon recovered.

Its action on a hard water may be shown by filling a wide tube (about 1″ in diameter) with permutit, one end being closed by a 1-hole rubber cork and tap delivery tube. A water containing 14 or 15 grains per gallon total hardness may be run fairly quickly over the material, when the hardness will be completely removed; this may be shown by adding 1 c.c. of soap solution to 70 c.c. of the filtered water when an abundant and permanent lather will be obtained on shaking.

Water for drinking purposes.

For drinking purposes, water must not be too soft, otherwise it is liable to attack the metal of the lead pipes. In cases of lead poisoning, it has been shown that this is generally due to an extremely soft water supply, and the remedy is usually to slightly harden the water. The lime and magnesium compounds retard the action of the water on the lead, about 3 or 4 grains per gallon of total hardness being sufficient to stop the action.

In the case of a very soft water, the action on the lead appears to be due to dissolved oxygen and carbon dioxide, first forming an oxide and hydroxide of lead, which then becomes carbonated, forming lead bicarbonate, slightly soluble in water and giving rise to lead poisoning The difference between hard and soft waters in this action may be shown by leaving two clean lead plates in distilled water and in a hard water respectively for about an hour. By the addition, at the end of that time, of a drop or two of ammonium sulphide solution to the distilled water, the lead in solution is easily detected by the formation of a dark brown coloration, whilst the hard water is unaffected if tested in a similar manner.

For drinking purposes, it is most essential that water must be free from even small quantities of organic matter. There is no simple direct method of estimating the amount of organic matter, and the purity of the water is measured by oxidising the nitrogenous organic matter with an alkaline solution of potassium permanganate. From the amount of oxygen consumed in a definite time, and from the amount of ammonia liberated when the water is distilled with the permanganate, the purity of the water may be ascertained. In judging a water for drinking purposes, these amounts are considered in conjunction with the amounts of sodium chloride, nitrates and nitrites in the water, these substances though harmless in themselves being indicative of previous organic contamination.

Most of the water supplies in England are taken from river water. This is first pumped or run into reservoirs for storing and settling, the greater portion of the coarse suspended matter being removed. The partially cleared water is then filtered, the usual method being to pass the water through layers of gravel and fine quartz or river sand, in specially constructed filters or filter beds. The suspended matter is thus practically entirely removed, the water is aerated, and the organic matter is also largely removed in the process. It is not so much the total amount of solid matter, as the character of the substances in solution, which class a water as a good or bad drinking water.

It is also essential that the water should be thoroughly aerated by containing dissolved gases, and these it generally contains in the form of dissolved atmospheric air.

Dalton and Henry's law of solubility of gases.

The solubility of gases in water varies very considerably, the solubility being expressed by the number of c.c.'s of gas dissolved by 1 c.c. of water at 0° C., this being termed the coefficient of solubility or of absorption of the gas.

The following are the coefficients of absorption of some of the common gases:

$$H=0{\cdot}0215;\ N=0{\cdot}0239;\ O=0{\cdot}049;\ CO_2=1{\cdot}713;\ Cl=3{\cdot}1;$$
$$H_2S=4{\cdot}68;\ SO_2=79{\cdot}8;\ HCl=506;\ NH_3=1300.$$

The solubility, however, varies with the temperature of the solvent, and is less in hot water than in cold.

The mass of gas dissolved by a definite volume of a given liquid is also proportional to the pressure of the gas ; this is known as Dalton and Henry's law of solubility of gases and may be expressed thus : "When the gas and solvent exert no chemical action upon each other, the volume of gas dissolved by a definite volume of liquid at any temperature is always the same and is independent of the pressure."

1 litre of water will dissolve 0·072 gram of O at 0° C. and 760 mm. pressure, and if the pressure is reduced to one-half, *viz.*, 380 mm., the amount dissolved, according to the law, will be 0·036 gram. But, according to Boyle's Law, 0·072 gram at 760 mm. and 0·036 at 380 mm. will occupy the same volume, *viz.*, 50 c.c.

The increased solubility, as represented by the increased mass of the gas dissolved with increased pressure, is shown in the solubility of CO_2 under pressure in aerated liquids.

CHAPTER XIV

FURTHER STUDY OF THE COMPOSITION OF WATER

ELECTROLYSIS AND IONISATION: IONIC THEORY: VOLUMETRIC COMPOSITION OF STEAM: LAW OF GAY LUSSAC: AVOGADRO'S HYPOTHESIS: GAS ANALYSIS: COMPOSITION OF WATER BY WEIGHT.

Composition of water by volume.

The composition of water may be determined both analytically and synthetically; in the former method the water is split up into its elements, whilst in the latter it is built up from its constituents.

Analytical method. The water is split up into its elements by a current of electricity, two or more accumulator cells being used or the apparatus may be connected in series with a set of incandescent lamps for drawing off the required amount of current from a lighting circuit. As water itself is practically a non-conductor of electricity, about 8 per cent. of its volume of sulphuric acid is added in order to make the liquid into a conductor.

The apparatus shown in Fig. 31, known as Hofmann's Voltameter, is employed, and is filled to the level of the taps with the acidified water or electrolyte. The platinum plates in the outer limbs are known as electrodes, the one where the current enters, or positive (+) electrode, is the anode, and the other, where the current leaves the liquid, the negative (−) electrode, or cathode. These plates are connected to platinum wires fused into and passing through the glass, and the wires on the outside are connected to the source of current, either directly or through the medium of mercury cups as in the figure.

The electrolyte is split up into hydrogen and oxygen, termed ions, the oxygen, being an electronegative element, is liberated at the anode, and is known as the anion, whilst the electropositive hydrogen is the cation.

By passing the current for some time, a quantity of gas may be collected, and two volumes of hydrogen will be obtained for each volume of oxygen, the accumulating gases driving the liquid from the outer limbs into the central store tube. Owing to the greater solubility of the oxygen, and the formation of small quantities of ozone and hydrogen peroxide, there is a slight loss in volume of free oxygen, but the volumes obtained are approximately correct.

Electrolysis. The process described above is known as electrolysis, and may be applied to most of the common inorganic acids, alkalis and salts, which are also electrolytes. The actual action taking place in the electrolysis of acidulated water is the decomposition of the free acid into hydrogen and sulphion (SO_4), the latter attacking water in a secondary reaction and re-forming sulphuric acid with the liberation of oxygen:

$$\begin{array}{ll} \text{Primary reaction:} & H_2SO_4 \rightarrow H_2 + SO_4 \\ \text{Secondary reaction:} & SO_4 + H_2O \rightarrow H_2SO_4 + O \end{array}$$

The molecules of acid thus begin to crowd round the anode, and the acidity of the liquid in this region increases.

Other acids, alkalis and salts, are broken up by electrolysis in a similar manner, the metals and hydrogen, being electropositive, are liberated at the cathode, whilst the electronegative acid radicals and hydroxyl are liberated at the anode.

$$\begin{array}{c} \text{Cathode }(-). \qquad\qquad \text{Anode }(+). \\ \text{electropositive}\left\{\begin{array}{l|l} H_2 & SO_4 \\ Na & OH \\ Na_2 & SO_4 \\ Cu & SO_4 \\ K & NO_3 \end{array}\right\}\text{electronegative} \\ \text{etc.} \end{array}$$

In the case of sodium sulphate, the following actions will take place:

$$\begin{array}{ll} \text{Primary reaction:} & Na_2SO_4 \rightarrow 2Na + SO_4 \\ \text{Secondary reactions:} & \left\{\begin{array}{l} 2Na + 2H_2O \rightarrow 2NaOH + H_2 \\ SO_4 + H_2O \rightarrow H_2SO_4 + O \end{array}\right. \end{array}$$

The action thus appears to be the decomposition of water, as hydrogen and oxygen are liberated, but sodium hydroxide accumulates round the cathode, the liquid becoming alkaline, and round the anode, the liquid becomes acid owing to the formation of sulphuric acid. If the two solutions round the respective electrodes are allowed to mix, the sodium sulphate molecules will be re-formed, and the decomposition thus appears similar to the electrolysis of water, H and O being the ultimate products.

Similar electrolytic actions are used in copper plating, nickel plating, electroplating and electrogilding, suitable electrolytes containing these metals being employed. Thus, by passing an electric current through a solution of copper sulphate, metallic copper is deposited on the metal forming the cathode, and sulphion (SO_4) is liberated at the anode, attacking a molecule of water to form sulphuric acid and oxygen gas.

$$\begin{array}{c} CuSO_4 \rightarrow Cu + SO_4 \\ SO_4 + H_2O \rightarrow H_2SO_4 + O \end{array}$$

Ionisation and modern theories of electrolysis. The ionic theory. In the experiments described above, the electrodes may be separated to a great distance in the electrolyte, or may even be in different vessels, if the latter are connected by a column of the electrolyte as shown in the figure, Fig. 44, and electrolysis will take place, yet there is no visible transference of the gases through the liquid.

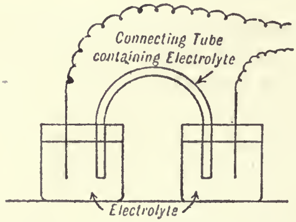


Fig. 44. Two electrolytic cells connected by syphon tube.

The modern theory of ionisation, which explains this fact, is that an electrolyte always exists in a partly broken up or dissociated condition, the liquid containing molecules of the electrolyte as well as the free ions. Thus in a solution of common salt or sodium chloride, the substance exists in the form of NaCl molecules, and Na and Cl ions, the number of the ions being increased as the liquid is diluted up to a certain maximum. These ions carry a definite charge, either positive or negative, of electricity, and in this respect differ from atoms, taking on the ordinary atomic properties when they lose their charges of electricity at the surface of the electrodes.

In order to distinguish the ions from atoms, the former are represented thus: Hydrion, $H^{\cdot}$, Chloridion, Cl', a dot being attached to each monad electropositive ion, and a single dash to the electronegative one; with diads, two dots or dashes are employed; with triads, three and so on.

Many facts relating to solutions, particularly dilute solutions, have been explained on the assumption that the molecules of electrolytes exist in dilute solution in a partially dissociated condition, which could not be previously accounted for, and the ionic theory has been so useful in this direction that there is no doubt that the assumption is a perfectly correct one.

Synthetical composition of water. The composition of water, by the synthesis of its constituent gases, may be shown by exploding together a mixture of hydrogen and oxygen in a suitable apparatus and measuring the volume of residual gas.

The apparatus shown in Fig. 45 may be employed, dry oxygen gas being passed into the tube, or Bunsen's eudiometer, which is graduated in millimetres. The volume of the gases throughout may be read in millimetres, and referred to as volumes. The temperature of the gas is taken by reading an adjacent thermometer, and the pressure of the gas is obtained by reading the levels of mercury in the tube and the trough on the millimetre scale, and subtracting the length of this column from the height of the barometer at the time.

Dry hydrogen is then passed into the tube, the volume, temperature, and pressure being similarly read off.

The mixture is exploded by passing an electric spark between the terminal wires fused through the closed end of the eudiometer, these wires being connected to the induction coil as shown. During the explosion, the tube may be wrapped in a duster and pressed down on to a rubber pad or cork under the mercury in the trough, to prevent the force of the explosion blowing the mercury out of the tube.

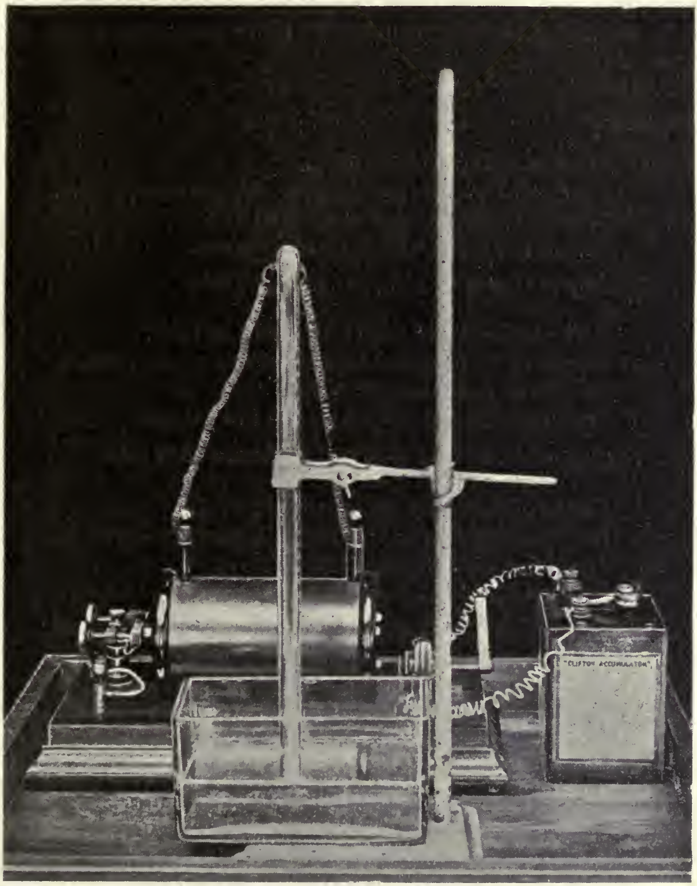


Fig. 45. The Bunsen eudiometer, for estimating hydrogen or oxygen in gaseous mixtures by explosion.

The hydrogen and oxygen will combine to form water, and the excess of hydrogen or oxygen is read off, together with the temperature and pressure, but as the gas will be saturated with water vapour, the pressure due to the water vapour at the temperature of the gas is deducted from the total pressure, so as to obtain the pressure of the dry gas.

All the volumes are then calculated to standard temperature and pressure (0° C. and 760 mm.), and the volumes of H and O combining may then be deduced, these being found to be in the proportion 2 vols. of H to 1 vol. of O.

Example:

112 vols. of O (moist) at 19° C.
Height of Hg column = 388 mm. Barometer = 756 mm.
Tension of H_2O vapour at 19° C. = 16 mm.
Pressure of gas = 756 − 388 − 16 = 352 mm.
∴ Volume of O at 0° C. and 760 mm. = 48·5 vols.

Volume of moist H and O = 285 vols. at 19° C.
Height of Hg column = 215 mm. Barometer = 756 mm.
Tension of H_2O vapour = 16 mm.
Pressure of H and O = 756 − 215 − 16 = 525 mm.
∴ Volume of H and O at 0° C. and 760 mm. = 184·1 vols.

Excess of H remaining = 90 vols. at 19° C.
Height of Hg column = 410 mm. Barometer = 756 mm.
Tension of H_2O vapour = 16 mm.
Pressure of H = 756 − 410 − 16 = 330 mm.
∴ Volume of dry H in excess = 36·5 vols. at 0° C. and 760 mm.

Volume of dry H taken = 184·1 − 48·5 = 135·6 vols. at N.T.P.
Volume of dry H combining with O = 99·1 vols. at N.T.P.
Volume of dry O combining with H = 48·5 vols. at N.T.P.
Volume of H : Volume of O :: 99·1 : 48·5 :: 2·04 : 1.

Volumetric composition of steam. The last experiment gives the volumes of H and O which combine together, but does not give the volume of steam formed in the reaction. This may be best obtained by exploding a mixture of 2 vols. of H and 1 vol. of O (electrolytic gas) in a special form of eudiometer, in which the resulting water is kept in the state of vapour by surrounding the eudiometer tube by a hot jacket. All the measurements are made at the temperature of the jacket and under atmospheric pressure.

The apparatus shown in Fig. 46 may be employed, this being a U-shaped eudiometer, with wires passing through the closed end for sparking the gas, and this part of the tube is surrounded by a jacket, *A*, through which toluene vapour (B.P. 110° C.) is passed to keep the water produced in the form of steam. The toluene vapour is passed in at the top of the jacket, and led off at the bottom to a condenser, *E*, for recovering the toluene liquid. The spark is passed by means of an induction coil, *C*, and accumulator, *D*.

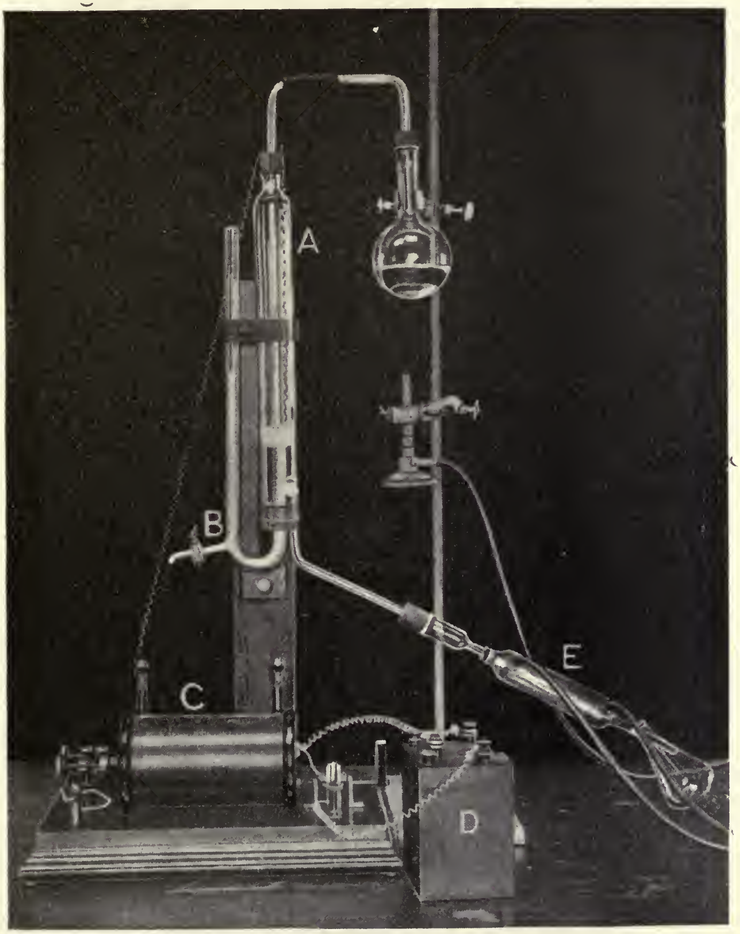


Fig. 46. **U**-shaped eudiometer for showing the volumetric composition of steam.

The open end of the **U**-shaped tube is provided near the bend with a tap, *B*, for running off mercury, so as to adjust the levels in the two limbs at the same height.

The eudiometer tube is first completely filled with mercury, which is then run off from the tap until the level of the mercury in the open limb is near the bend of the tube. By means of a long delivery tube, with a short piece of rubber tubing attached, to pass round the bend of the tube, a convenient quantity of electrolytic gas may be passed into the closed limb. The levels of mercury are adjusted to the same height after the closed limb has been heated to the temperature of the toluene vapour, and the volume of the gas is then noted.

An electric spark is passed between the terminal wires, the open end being meanwhile closed by the thumb to enclose air which acts as a buffer, and prevents loss of gas by the mercury being blown round the bend. The levels are again adjusted to the same height by pouring in mercury, and the volume of steam will be found to be two-thirds of the original volume, under similar conditions of temperature and pressure. The experiment thus proves that 2 vols. of H combine with 1 vol. of O to form 2 vols. of steam.

Gay Lussac's law of volumes. From a number of experiments similar to the above, Gay Lussac deduced the following law: "In gaseous reactions, the volumes of the gases reacting together, as well as the volumes of the gases formed, bear a simple relation one to the other."

Thus, 1 vol. of H combines with 1 vol. of Cl to form 2 vols. of HCl; 1 vol. of N combines with 3 vols. of H to form 2 vols. of ammonia, and, as already shown, 2 vols. of H combine with 1 vol. of O to form 2 vols. of steam.

Avogadro's hypothesis. Avogadro gave the true explanation of the above facts in his hypothesis, which states that "equal volumes of all gases, under similar conditions of temperature and pressure, contain an equal number of molecules."

It follows from this hypothesis, that the proportions by volume in which gases combine together, and the volumes of gases formed, give the proportions of the number of molecules reacting and formed; thus the reactions given above may be expressed by the following equations:

$$\begin{array}{ccccc} 2H_2 & + & O_2 & \rightarrow & 2H_2O \\ \text{2 mols.} & & \text{1 mol.} & & \text{2 mols.} \\ \text{2 vols.} & & \text{1 vol.} & & \text{2 vols.} \end{array}$$

$$\begin{array}{ccccc} H_2 & + & Cl_2 & \rightarrow & 2HCl \\ \text{1 mol.} & & \text{1 mol.} & & \text{2 mols.} \\ \text{1 vol.} & & \text{1 vol.} & & \text{2 vols.} \end{array}$$

$$\begin{array}{ccccc} N_2 & + & 3H_2 & \rightarrow & 2NH_3 \\ \text{1 mol.} & & \text{3 mols.} & & \text{2 mols.} \\ \text{1 vol.} & & \text{3 vols.} & & \text{2 vols.} \end{array}$$

Whenever an equation is written in molecular form, we may obtain, from the number of molecules of gases reacting, the relationship between the volumes of the gases either taking part in the reaction or the volumes of the gases formed.

Gas analysis. These facts are made use of in the analysis of gaseous mixtures; thus to estimate the amount of O in a mixture, such as air, an excess of H may be mixed with the air and the mixture exploded. The whole of the O will combine with some of the H and condense as liquid water, 1 vol. of O combining with 2 vols. of H, so that $\frac{1}{3}$ of the gas disappearing as liquid water is the oxygen present in the volume of air taken.

Similarly H may be estimated in a mixture, such as a gaseous fuel, by mixing with an excess of O and exploding. In this case $\frac{2}{3}$ of the disappearing gas gives the volume of H.

Marsh gas, or methane, CH_4, which is an important constituent of coal gas, and which is the main constituent of "fire damp" in coal mines, may be also estimated by explosion with an excess of O, the following action taking place:

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} \rightarrow \underset{\text{1 vol.}}{CO_2} + \underset{\substack{\text{2 vols. steam}\\\text{(condensing to water)}}}{2H_2O}$$

In this case 1 vol. of methane produces 1 vol. of carbon dioxide, and the latter is readily estimated by absorption of the gas by means of caustic potash, the volume of CO_2 absorbed giving the volume of methane in the original measured volume of the mixture exploded with oxygen.

Composition of water by weight.

The composition of water by weight was carried out with a remarkable degree of accuracy by the famous French chemist, Dumas, who made use of the fact that when hydrogen is passed over heated copper oxide, the oxygen of the copper oxide combines with the hydrogen to form water. The hydrogen, prepared from zinc and sulphuric acid, usually contains traces of the following impurities: sulphuretted hydrogen, arseniuretted hydrogen, carbon dioxide, sulphur dioxide and water vapour. It is of the greatest importance in this experiment that the hydrogen should be pure and dry, and this is secured by passing the gas through a series of U-tubes (Fig. 47), containing reagents for the absorption of the impurities thus:

(A) **U**-tube containing solid lead nitrate for absorption of H_2S:

$$Pb(NO_3)_2 + H_2S \rightarrow PbS + 2HNO_3$$

(B) **U**-tube containing solid silver nitrate for absorption of traces of AsH_3:

$$6AgNO_3 + 3H_2O + AsH_3 \rightarrow \underset{\text{arsenious acid}}{H_3AsO_3} + 6HNO_3 + 6Ag$$

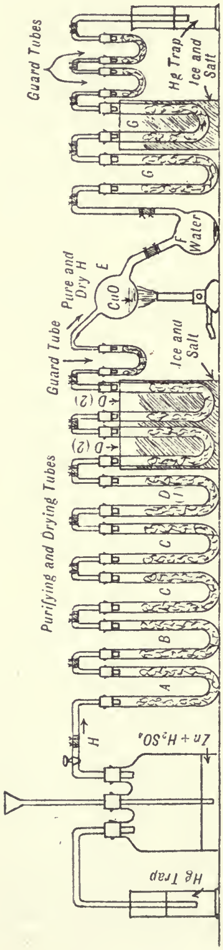


Fig. 47. Dumas' experiment on composition of water by weight.

(C) **U**-tubes containing solid caustic potash for absorption of CO_2, SO_2 and traces of HNO_3 formed in (A) and (B):

$$CO_2 + 2KOH \rightarrow K_2CO_3 + H_2O$$
$$SO_2 + 2KOH \rightarrow K_2SO_3 + H_2O$$
$$HNO_3 + KOH \rightarrow KNO_3 + H_2O$$

(D) **U**-tubes containing (1) pumice moistened with concentrated sulphuric acid and (2) phosphorus pentoxide, for thoroughly drying the gas.

Finally the gas is passed through a small weighed tube, containing phosphorus pentoxide, termed a guard tube; in all experiments which are considered reliable ones, this tube must remain constant in weight, indicating that the hydrogen has been thoroughly dried. The pure and dry hydrogen is passed through a weighed bulb, *E*, containing pure copper oxide, previously ignited to remove traces of water, and after the experiment the bulb, *E*, is cooled, the hydrogen remaining in it is displaced by air and the bulb again weighed. The loss in weight gives the amount of oxygen combining with the hydrogen to form water. The water formed is carefully collected in a bulb, *F*, and any moisture carried on by the excess of hydrogen is collected by passing through a series of drying tubes, *G*, and guard tube, similar to those used at *D* for drying the hydrogen.

The second guard tube prevents backward diffusion of moisture, in case there should be any backward diffusion of air. Mercury traps are used at each end, and as the delivery tube is deeper in the mercury in the trap attached to the Woulff's bottle, the excess of gas only passes through this trap when the tap in the delivery tube is partially closed to regulate the speed of the gas through the **U**-tubes.

The bulb, *F*, and tubes, *G*, are accurately weighed before and after the experiment, the increase in weight giving the weight of water formed. By subtracting the weight of oxygen used (*i.e.*, the loss in weight of the copper oxide bulb) from the weight of water formed, the weight of hydrogen combining with oxygen is obtained; and the amount of oxygen combining with 1 gram or 1 part by weight of hydrogen is easily calculated.

The following figures were obtained by Dumas in one of his experiments:

grams
Weight of the copper oxide tube *before* the experiment = 334·598
" " " " *after* " " = 314·236
Loss in weight (= oxygen) = 20·362

Bulb and drying tubes *after* the experiment = 449·263
" " " *before* " " = 426·358
Gain in weight (= water) = 22·905

22·905 − 20·362 = 2·543 grams = weight of hydrogen.

Hence the proportion of oxygen to hydrogen by weight is

20·362 : 2·543 or 88·88 °/o : 11·12 °/o = 7·94 : 1 or 15·88 : 2,

and is represented by the formula H_2O. Relatively to hydrogen = 1, the atomic weight of oxygen will be 15·88, or as O = 16 (International Atomic Weights) is usually taken as the standard, this will give an atomic weight for H = 1·008.

CHAPTER XV

HYDROGEN PEROXIDE AND OZONE

HYDROGEN PEROXIDE: PREPARATION, MANUFACTURE: DISTILLATION UNDER REDUCED PRESSURE: HYDROGEN PEROXIDE FOR BLEACHING PURPOSES: CONTACT ACTION: DETECTION AND ESTIMATION OF HYDROGEN PEROXIDE: OZONE: ALLOTROPY: USES IN PURIFICATION OF AIR, WATER, ETC.

Hydrogen peroxide.

Hydrogen peroxide, or hydroxyl, is of great importance in textile industries, as it is now largely used as a bleaching agent, and particularly in the treatment of wool.

Occurrence and formation. It occurs in minute traces in the atmosphere, and is produced in small amount in the electrolysis of water and in the burning of hydrogen in air.

Preparation. The compound can be obtained by the action of carbon dioxide upon barium peroxide, suspended in ice-cold water, thus:

$$BaO_2 + CO_2 + H_2O \rightarrow BaCO_3 + H_2O_2$$

A more usual way of preparing it is to add the barium peroxide to dilute ice-cold sulphuric acid, until the liquid is only slightly acid, the clear liquid being finally neutralised by a solution of barium hydroxide.

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$$
$$Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2H_2O$$

After filtering off the insoluble barium sulphate, a dilute solution of hydrogen peroxide is obtained.

Hydrogen peroxide can also be prepared by the action of sodium peroxide on ice-cold dilute hydrochloric acid, but in this case the solution also contains sodium chloride, though this is not objectionable for most purposes for which the hydrogen peroxide is required, and the method is a ready one for preparing small quantities for laboratory use.

$$Na_2O_2 + 2HCl \rightarrow H_2O_2 + 2NaCl$$

Manufacture. It is obtained on a large scale by the action of barium peroxide on ice-cold dilute sulphuric acid, as described above, or by the use of phosphoric or hydrofluosilicic acid, a slight trace of the acid left in the liquid aiding its preservation; the acids must be dilute and kept cool by ice during the action.

$$3BaO_2 + 2H_3PO_4 \rightarrow 3H_2O_2 + Ba_3(PO_4)_2$$
$$BaO_2 + H_2SiF_6 \rightarrow H_2O_2 + BaSiF_6$$

Purification. Attempts to concentrate the H_2O_2 by ordinary methods of distillation result in its decomposition, and it can only be concentrated either in a vacuum or by distillation under reduced pressure.

For this purpose the liquid is put into a distilling flask, *A*, Fig. 48, which is connected by a rubber cork to a second flask, *B*, for receiving the distillate, the latter flask being connected by a water pump, *D*, and manometer, *C*, for reducing and registering the pressure. The distillation flask is provided with a tube drawn out to a fine point, so that by means of a clip a stream of fine air bubbles is admitted to prevent bumping of the liquid, and by means of a thermometer the temperature is noted.

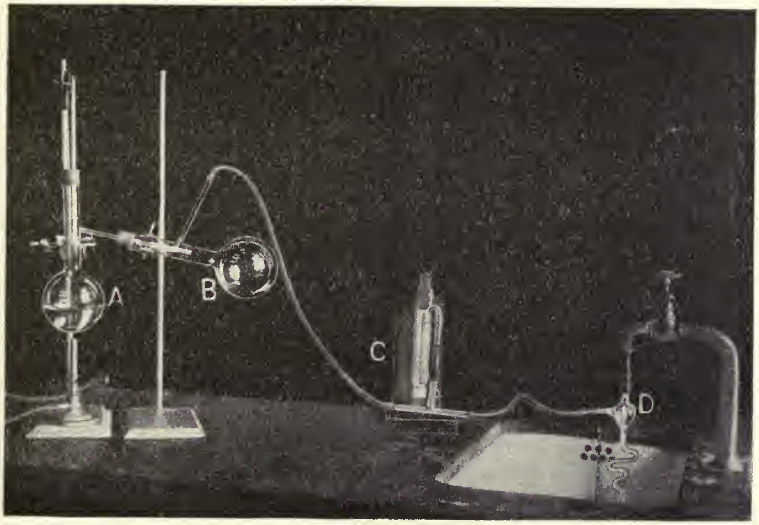


Fig. 48. Distillation under reduced pressure.

The pressure is reduced by the pump until the manometer registers about 15 mm. and the distillation is commenced, a slow stream of air being admitted. Water with a little H_2O_2 distils over, and the temperature gradually rises until, at 70° C., a moderately concentrated solution of hydrogen peroxide remains in the distilling vessel.

This may be finally concentrated in a vacuum desiccator, containing concentrated sulphuric acid, the acid absorbing the water, which gradually vaporises from the solution until finally pure hydrogen peroxide remains.

Properties. The pure liquid is colourless and has a somewhat metallic taste; it is very unstable and gradually evolves oxygen, even at $-20°$ C.; when warmed the liquid rapidly gives up oxygen, and the gas is evolved explosively at 100° C.

It is more commonly sold in the form of a solution, the strength being stated from the number of volumes of oxygen which can be obtained from one volume of the liquid. The common strengths sold are "10 vols.," "14 or 15 vols.," and "20 vols.," hydrogen peroxide. The oxygen is evolved readily from solutions of these strengths by heating, preferably by making the liquid slightly alkaline with caustic soda, and the oxygen may be collected in the ordinary way over water. The peroxide is much less stable in alkaline solution, and, as already mentioned, it is usually, in commerce, slightly acid. It has also been shown that small quantities of alcohol, ether, glycerol and oxalic acid confer stability on the liquid. In medicinal preparations 1 per cent. of sodium or calcium chloride is more commonly used.

The molecule may be looked upon as water with an additional atom of oxygen loosely held, and the ease with which this oxygen is evolved results in the hydrogen peroxide acting as a powerful oxidising agent. Thus it will oxidise lead sulphide (black) to lead sulphate (white):

$$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$$

This can readily be shown by pouring a solution of lead acetate over a sheet of paper, exposing it to the action of sulphuretted hydrogen gas, and then drying the paper. In this way lead sulphide is deposited in a thin black layer on the surface of the paper. By painting the paper with a solution of hydrogen peroxide the black colour is immediately discharged, owing to the oxidation of the lead sulphide to white lead sulphate, as shown in the equation above. This reaction has a practical application in renovating oil paintings darkened by age; in such cases the white lead, used to give "body" to the paint, has gradually been darkened by the action of traces of sulphur compounds in the atmosphere, but by treatment with hydrogen peroxide white lead sulphate similar to the original white lead is formed.

Use of hydrogen peroxide for bleaching purposes. Hydrogen peroxide finds an important practical application in the bleaching of fibres, where bleaching powder cannot be used; thus fibres of the wool class are readily bleached by means of a solution of hydrogen peroxide. As hydrogen peroxide is much more stable in acid than in alkaline solution, the liquid is usually rendered alkaline by the addition of a small quantity of ammonium hydroxide, when it is to be used for bleaching purposes.

Sodium silicate is sometimes used to supply the alkali, the wool being steeped in a 2 per cent. solution previous to the immersion in the bleaching bath. The bleaching baths usually contain about 30 per cent. of 10 vol.

hydrogen peroxide and ·5 per cent. sodium silicate, the wool being allowed to remain in this bath for about 24 hours at 80° F. When the bleaching is complete, the alkali, which would have a detrimental effect on the fibre, is removed by treatment with very dilute sulphuric acid.

When wool has been bleached by sulphur dioxide, in the process usually known as "stoving," the last traces of sulphur dioxide are sometimes removed by washing with a dilute solution of hydrogen peroxide. This prevents fading in the dyed fabric, which might result through sulphur dioxide being left in the fabric.

Hydrogen peroxide bleaches wool a purer white than is obtained with sulphur dioxide, and does not tender the fabric to the same extent. The wool, after bleaching, does not turn yellow, and does not give an unpleasant odour when in contact with perspiration.

Silk may be similarly bleached, without loss of gloss, elasticity or strength, by hydrogen peroxide, and feathers, hair, etc., previously cleansed with soap solution or with petroleum spirit, for removing grease or natural fat, may also be bleached by means of a faintly alkaline peroxide solution. It may also be used as a detergent, but, when used for this purpose, care must be taken in cases where the peroxide is employed on dyed fabrics, or the material will lose some of its colour.

Action on metallic oxides and metals. Contact action. If silver oxide is added to a solution of hydrogen peroxide, the silver oxide is reduced to silver, the hydrogen peroxide to water, and oxygen is liberated with effervescence.

$$Ag_2O + H_2O_2 \rightarrow 2Ag + H_2O + O_2$$

Similarly manganese dioxide is reduced to manganese monoxide:

$$MnO_2 + H_2O_2 \rightarrow MnO + H_2O + O_2$$

Finely divided metals, such as silver and platinum, will bring about the decomposition of hydrogen peroxide by contact only, and these actions come under the class already referred to as catalytic actions, though they are frequently known as "contact actions." It is probable that two atoms of the metal are first oxidised by a molecule of hydrogen peroxide, the molecule of oxide formed being then reduced by a second molecule of hydrogen peroxide, thus:

$$\begin{aligned} H_2O_2 + 2Ag &\rightarrow Ag_2O + H_2O \\ H_2O_2 + Ag_2O &\rightarrow H_2O + 2Ag + O_2 \end{aligned}$$

One loose atom of oxygen in one molecule is thus apparently oxidising a second atom of oxygen, in a second molecule of H_2O_2, to the molecular condition.

Estimation of strength of peroxide solutions. If a solution of hydrogen peroxide containing H_2SO_4 is treated with a solution of potassium permanganate, it is reduced to water, the permanganate to potassium and manganese sulphates, which are practically colourless, and oxygen is liberated. The end of the reaction is denoted when the colour of the permanganate is permanent. Thus if a solution of potassium permanganate of known strength is used and the volume of this solution, required to produce a permanent pink colour when added to a definite volume of hydrogen peroxide, is obtained, the amount of permanganate used can be made a measure of the amount of hydrogen peroxide in the solution and the strength of the hydrogen peroxide can be obtained.

This is the method usually used for estimating the strength of solutions of hydrogen peroxide:

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow 5O_2 + 8H_2O + K_2SO_4 + 2MnSO_4$$

The evolution of oxygen in this action may be shown by dropping a solution of hydrogen peroxide, acidified with sulphuric acid, on to solid potassium permanganate, and the strength of the hydrogen peroxide may be roughly estimated by halving the volume of oxygen obtained.

Detection of hydrogen peroxide in solution. Potassium iodide is decomposed by a solution of hydrogen peroxide with the liberation of iodine, which may be detected by the formation of the deep blue iodide of starch on addition of a starch solution.

$$2KI + H_2O_2 \rightarrow 2KOH + I_2$$

Hydrogen peroxide, when present in a very dilute solution, may be detected by adding the liquid to a dilute solution of potassium dichromate, acidified with dilute hydrochloric acid. A deep blue unstable compound is obtained, which is probably perchromic acid, $2CrO_3$, H_2O_2. In the case of very dilute solutions, the colour is best detected by shaking the liquid with ether, in which the blue compound is more soluble; the lighter ether layer is then coloured a deep blue, and in this way it is possible to detect 1 part of H_2O_2 in 200,000 parts of water.

Ozone.

Allotropy. Certain elements, such as oxygen, sulphur, carbon, phosphorus, etc., are found to exist in more than one form, the various forms possessing different physical properties. These different forms of the same element are termed allotropic modifications, and are said to exhibit the property of allotropy.

In the case of oxygen and ozone, it is known that the difference is due to a difference in molecular structure, the molecules of these substances being O_2 and O_3 respectively, but the origin of the differences in other cases is not known, though it is also probably due to differences in structure of the molecules.

Formation. Whenever electric sparks are produced in air or oxygen a portion of the oxygen is converted into ozone, and a peculiar smell is observed in the region of the electrical machine, though the cause of the formation is not understood. As only a very limited amount of gas can be passed through electric sparks, and the temperature of the spark is also sufficient to re-convert the ozone into oxygen, this forms a very inefficient way of producing ozone.

Preparation. A far better method of preparing ozone, and one which is now used on a large scale, *e.g.*, in all the forms of ozonisers put on the market, is to submit the oxygen or air to the action of the silent electric discharge from a high tension current, such as that obtained from the secondary of an induction coil or transformer.

If the secondary terminals of such a coil be connected to two metallic plates, a slow and silent discharge takes place between the metallic surfaces, resulting in a moderate percentage of the oxygen being converted into ozone. It is necessary, however, to remove the gas moderately rapidly from the scene of the action, and to keep the metallic surfaces of the electrodes cool in order to obtain a good yield.

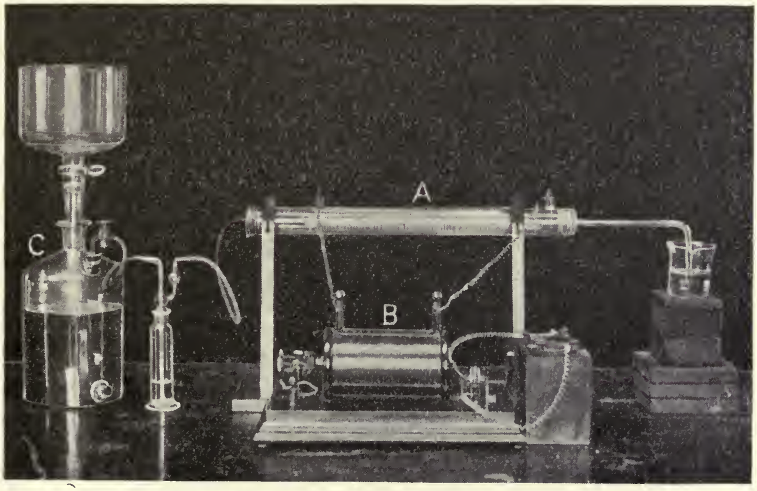


Fig. 49. Modern form of ozoniser.

One of the earliest forms of ozonisers was that known as Siemens' ozoniser, in which oxygen was passed through the annular space between two concentric glass tubes, the inner and outer tubes being respectively lined and coated with tinfoil, and these metallic surfaces are connected to the secondary terminals.

A more modern form of ozoniser is shown in Fig. 49, the inner electrode being an aluminium rod inside a vacuous tube, and the second electrode consists of a number of aluminium discs, each with an inner serrated edge, fitting round the inner tube. The discs are connected together by overlapping aluminium strips to form one single electrode, and the whole is contained in a tube, *A*, through which dry oxygen is slowly passed from the gasholder, *C*. Two precautions are necessary, namely, the drying of the oxygen or air in order to increase the yield, and the importance of avoiding indiarubber tube connections, as ozone rapidly combines with rubber.

The serrated edge, by providing a number of points, aids the discharge of the electricity which is produced between the electrodes by the induction coil, *B*.

Chemical method of preparing ozone. Ozone is also formed to a small extent, when phosphorus is allowed to undergo slow oxidation in moist air or oxygen, and is nearly always formed during the evaporation of water. This latter fact may account for the presence of ozone in the atmosphere over the sea and in the country generally, or it may have been produced by the discharges of atmospheric electricity.

Ozone is very active, and will bring about many actions that cannot be carried out with oxygen. The change from oxygen to ozone is due to a change in the number of atoms in the molecule. Oxygen contains two atoms in the molecule and is expressed O_2; ozone contains three atoms in the molecule and is expressed O_3.

Properties and uses. Ozone is an invisible gas with a pungent odour. It is a powerful oxidising agent and will oxidise mercury at the ordinary temperature. If a globule of mercury is allowed to run over the inner surface of a clean flask containing a little ozone, the mercury adheres to the sides of the vessel, forming a mirror, and eventually becomes coated with a thin yellowish layer of oxide. Ozone will oxidise black lead sulphide to white lead sulphate, and if lead suphide paper (prepared as described under hydrogen peroxide) is brought into contact with ozone the black colour is rapidly discharged. The gas liberates iodine from a solution of potassium iodide, and if a little starch paste* is added the deep blue colour of the starch iodide makes the change much more apparent.

$$2KI + O_3 + H_2O \rightarrow I_2 + 2KOH + O_2$$

Since ozone is a powerful oxidising agent, it destroys many colouring matters and acts as a bleaching agent. If ozone is allowed to bubble through a solution of indigo the blue colour very soon disappears.

The so-called "**ozone water**" which is sometimes met with in commerce does not contain any ozone but is usually a solution of hypochlorites, hydrogen peroxide, etc. It is used as a bleaching agent.

Ozone on heating to 250° C. is converted back into oxygen. When oxygen is converted into ozone there is a decrease in volume, so that ozone has a greater density than oxygen. When the ozone is reconverted into oxygen on heating, the original volume of oxygen is obtained.

Ozonised air is now used on a large scale for destroying noxious smells arising during various manufacturing processes, and is also used as an oxidising and sterilising agent in disinfecting and ventilating public buildings, theatres, etc., and in the purification of water for drinking purposes.

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* A clear solution of starch paste can easily be prepared by crushing a piece of starch the size of a pea, shaking with a few c.c.'s of water and heating in a test tube till the starch granules are broken up. The hot syrupy liquid is poured into a beaker containing about 100 c.c. of cold water.

CHAPTER XVI

NITROGEN AND THE ATMOSPHERE

Atmospheric and chemical nitrogen: More detailed study of the composition of the atmosphere: Analysis of air: Hempel's method: Carbon dioxide in air and its estimation: Ventilation: Haldane's apparatus for the estimation of carbon dioxide in the air of factories: Moisture in air and its estimation: Hygrometry: Conditioning of textile materials.

Nitrogen.

Nitrogen: Symbol, N; atomic weight, 14.

Atmospheric and chemical nitrogen. There are two chief groups of methods by which nitrogen can be prepared; (1) from the atmosphere by removing the oxygen; (2) from a number of compounds containing nitrogen, which under certain conditions may be decomposed with the liberation of nitrogen. The gas obtained from the former methods is known as "atmospheric nitrogen" and, from the latter, "chemical nitrogen."

In a research on the density of nitrogen in which some very accurate experiments were made, Lord Rayleigh found that the density of atmospheric nitrogen differed very slightly from that of nitrogen prepared by chemical means. After careful investigation, it was found that the difference was due to the presence, in atmospheric nitrogen, of small traces of other gases similar in properties to nitrogen, and the chief of these was a gas which Rayleigh named argon.

Atmospheric nitrogen: preparation. Atmospheric nitrogen can readily be prepared by passing air over heated copper, the oxygen of the air combining with the copper and the nitrogen passing on (see p. 24).

Chemical nitrogen: preparation. Chemical nitrogen is best prepared by gently heating ammonium nitrite. This substance is not very stable, and it is best prepared at the time it is required, by dissolving molecular proportions of ammonium chloride and sodium nitrite in a small quantity of water.

$$\underset{\underbrace{14+4+35{\cdot}5}_{53{\cdot}5}}{NH_4Cl} + \underset{\underbrace{23+14+32}_{69}}{NaNO_2} \rightarrow NaCl + NH_4NO_2$$

The apparatus required is similar to that used in the preparation of oxygen from potassium chlorate and manganese dioxide, with the exception that the flask is used in an upright position. A convenient strength of solution to use consists of 10 grams of NH_4Cl and 15 grams of $NaNO_2$ dissolved in about 150 c.c. of water, the liquid being gently heated and the gas collected over a pneumatic trough. The flame should be removed as soon as the evolution of the gas is moderately rapid, as the heat formed in the combination of the salts is sufficient to bring about the decomposition of the ammonium nitrite. Occasionally the speed of the reaction becomes so great, owing to the solution being too strong, as to be unmanageable, and the liquid in the flask froths up and passes through the delivery tube. The reaction may be slackened by cooling the flask with a dish of cold water. If the reaction stops, the flask should be gently heated; the following reaction takes place:

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

Properties. Free nitrogen is a very inert gas and its properties are therefore of a negative character. It does not support life and combustion, it does not burn, it has no colour, taste, nor smell, and is almost insoluble in water. Although nitrogen does not combine with oxygen under ordinary conditions it can be made to unite by submitting a mixture of the two gases to a series of electric sparks. However, since the oxides of nitrogen which are produced are decomposed at the high temperature of the electric spark only small quantities of nitrogen oxides are obtained, unless they are cooled and removed from the region of the spark immediately they are formed. Various forms of apparatus have been devised for producing these conditions and the process is now carried out on the commercial scale, particularly where water power is available for the cheap generation of the powerful electric current required. These oxides of nitrogen can be converted into valuable products such as nitric acid and sodium nitrite which will be dealt with in a subsequent chapter.

Formation of ammonia from nitrogen and hydrogen. If a series of electric sparks is passed through a mixture of three volumes of hydrogen and one volume of nitrogen, about 2 per cent. is converted into ammonia, but if the pressure is increased the percentage of ammonia which is formed is greater in amount.

Still better results can be obtained by treating this mixture of hydrogen and nitrogen at 150 atmospheres pressure and 500° to 700° C. with a catalyst such as powdered osmium or platinum. The ammonia is separated from any unchanged hydrogen and nitrogen by passing the gases through tubes immersed in a freezing mixture, when the ammonia condenses to a liquid, and the nitrogen and hydrogen pass on and can be again treated with the catalyst.

The atmosphere.

Composition of air. It has already been shown by rough experiments, that the air consists of a mixture of approximately one volume of oxygen and four volumes of nitrogen.

The analysis of samples of air from different parts of the world shows that the relative proportions of oxygen and nitrogen are almost constant; the amounts of some of the other gases may vary within fairly considerable limits according to the atmospheric conditions and the locality in which the sample is taken. The following is the volume composition of a fairly average sample of air:

Oxygen	Nitrogen	Argon	Carbon dioxide	Water vapour	Other gases, ammonia, nitric acid, ozone, etc.
20·5 °/o	77·0 °/o	·9 °/o	·04 °/o	1·56 °/o	traces

Hempel's apparatus. Many forms of apparatus have been devised for the accurate analysis of air, but only the Hempel apparatus need be dealt with, as this is the one largely used in technical work, and practically forms the basis on which the other forms are constructed. It affords a means of obtaining a quick and sufficiently accurate analysis of a mixture of gases.

The apparatus consists of two chief parts: the burette, used for measuring the gases, and the pipette, which is used for absorbing the constituents of the mixture.

The burette. This consists of a long, graduated measuring tube (Fig. 50) terminating at the top in a capillary tube and tap, and connected at the bottom to the levelling or pressure tube. The burette is usually made to hold 100 c.c. of gas and is graduated in $\frac{1}{10}$ c.c.'s, usually with two scales, one reading up and the other down. The burette may be constructed with an additional three-way tap at the bottom for adding or running off the liquid, or for passing a stream of gas through the measuring tube.

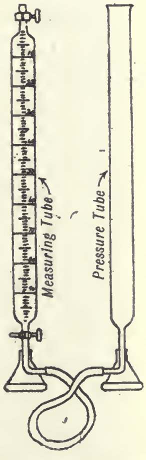


Fig. 50. Hempel burette.

The absorption pipette. This consists of a tube with two bulbs as shown in the diagram (Fig. 51), each bulb having a volume of about 120—150 c.c., and partly filled with liquid through the open end of the store bulb, *b*.

Analysis of air by the Hempel apparatus. The burette is first filled with liquid to the level of the tap by raising the pressure tube, and the sample of gas to be analysed is drawn in through the tap by lowering the pressure tube.

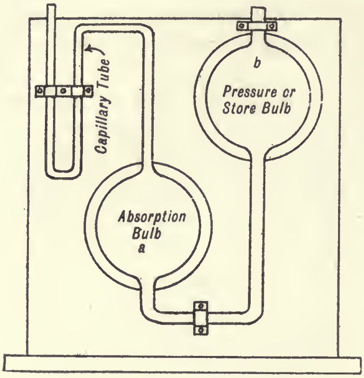


Fig. 51. Hempel pipette.

A sample of air from the room may be drawn into the burette in this way, and the volume of air adjusted so that 100 c.c. are taken when the levels of liquid in the measuring and pressure tubes are at the same height.

All readings are taken, in this way, with the gas under a pressure equal to that of the barometer.

For estimating carbon dioxide in a gaseous mixture, a potash pipette is used containing a 30 per cent. caustic potash solution, but as the amount of CO_2 in air is so small, special forms of apparatus are constructed to estimate accurately the amount of CO_2, and these will be dealt with later in this chapter.

The oxygen in the air is estimated by employing a pipette containing an alkaline solution of pyrogallic acid, 20 grams of pyrogallic acid being dissolved in 200 c.c. of a 30 per cent. potash solution.

The pyrogallic acid solution may be employed in a double pipette as shown in the sketch (Fig. 52), the pair of bulbs (*c* and *d*) nearer to the outside atmosphere containing water and thus forming a water seal to keep the "pyro" solution in the bulbs *a* and *b* out of contact with the outside atmosphere, a method used for preserving the strength of the liquid.

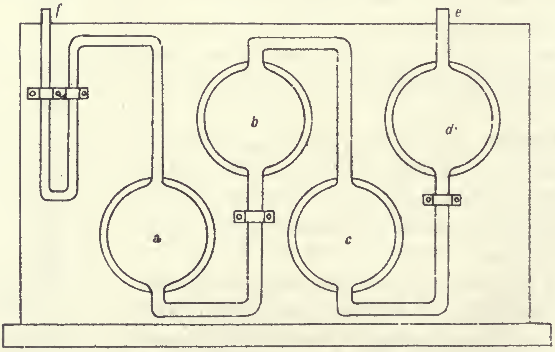


Fig. 52. Hempel double pipette.

To use the apparatus, any gas in the pipette is first drawn out and the bulb *a* filled with "pyro" solution. The capillary tube of the pipette is then connected to the burette by a piece of capillary tubing bent twice at right angles, and the rubber joints wired on with copper wire (Fig. 53).

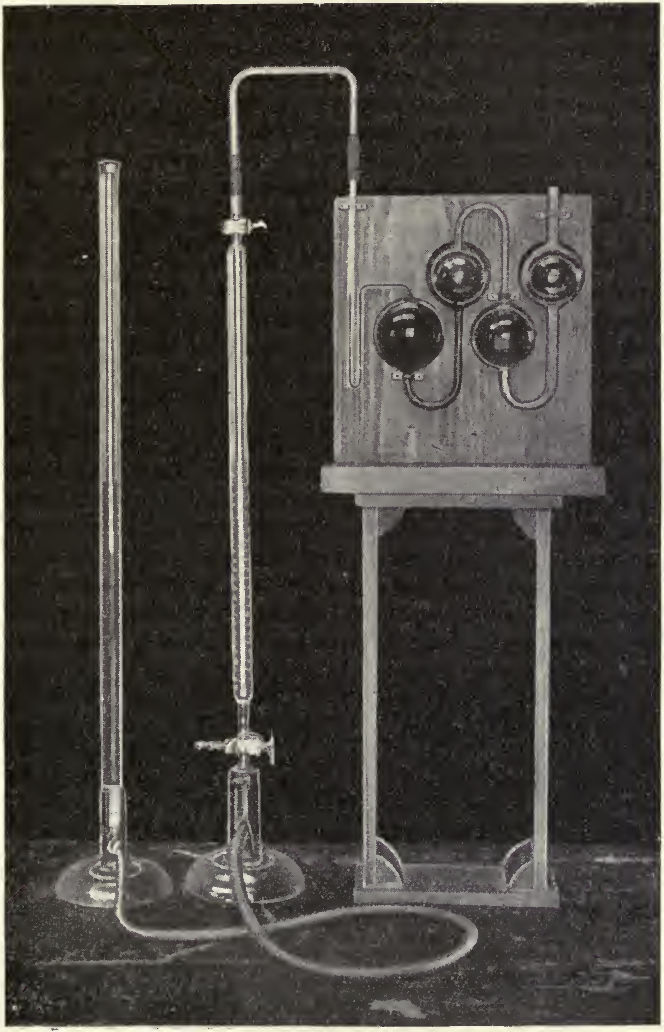


Fig. 53. Hempel burette and pipette fixed up in working position.

The tap is opened and the pressure tube raised until the air is all driven over into the pipette, the tap closed, and the gas is left in contact with the "pyro" solution for about five minutes, the pipette being preferably gently shaken at intervals. By again opening the tap and lowering the pressure tube the gas is drawn back into the measuring tube of the burette, care being taken not to get any of the "pyro" solution into the tap tube.

The volume of oxygen absorbed is then read off on the vertical scale. reading upwards from zero, and as 100 c.c. of air were taken, the reading gives the percentage of oxygen. The percentage of nitrogen, which is always obtained by difference after removing all other gases, is read off on the scale, reading from zero downwards.

It is always preferable to pass the gas again over into the pipette and, after a short interval, draw it back into the burette and measure it. This should be repeated until two consecutive readings agree, indicating that all the oxygen has been absorbed.

Carbon dioxide in air. If a clear solution of lime water is exposed in a shallow dish to the air for some time, a white scum forms on the surface of the liquid. If this scum is analysed, it is found to consist of calcium carbonate, and is identical with the substance obtained on shaking carbon dioxide with lime water. The amount of carbon dioxide, by volume, which is present may be determined by the following method.

Estimation of carbon dioxide in air. Air is first dried by drawing it through tubes containing granulated anhydrous calcium chloride, and it is then passed through weighed bulbs containing a 30 per cent. solution of caustic potash which absorbs the carbon dioxide. A known volume of air is passed slowly through the apparatus by allowing a known volume of water to flow from an aspirator as shown in the diagram (Fig. 54). When about ten litres of air have been passed, the current of air is stopped and the potash bulbs disconnected, and again weighed. The increase in

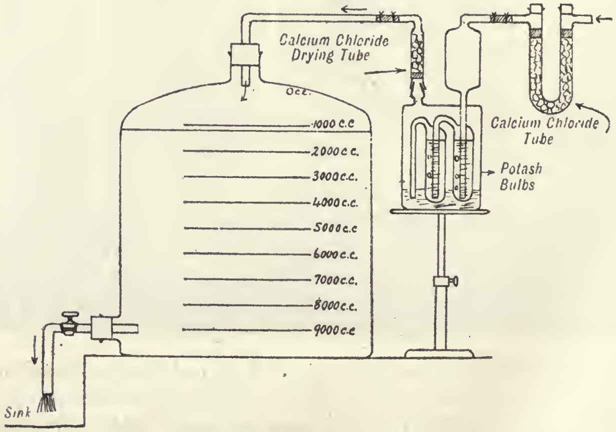


Fig. 54. Estimation of carbon dioxide and moisture in air. (The potash bulbs are enlarged.)

weight gives the amount of carbon dioxide in the volume of gas used. A small drying tube is attached to and weighed with the potash bulbs, to avoid the error which would be obtained through the dry air carrying moisture away from the potash solution.

Estimated in this way, the air is found to contain about 0·03 per cent. or 3 volumes of carbon dioxide in 10,000 volumes of air. In crowded districts and particularly in crowded rooms, factories, mines, etc., the proportion of carbon dioxide increases. The chief sources of this carbon dioxide are the following:

(1) The combustion of coal, coke, wood, oil, etc. and all substances containing carbon.

(2) The various forms of animal life convert part of the oxygen, taken into the body through the lungs, into carbon dioxide, and consequently the air expired from the lungs is richer in carbon dioxide than inspired air.

(3) In many manufacturing processes, *e.g.*, the production of quicklime from limestone, the manufacture of alcohol by fermentation, etc., large volumes of carbon dioxide are evolved.

Balance between amounts of oxygen and carbon dioxide in air. From the causes mentioned, the amounts of carbon dioxide in the atmosphere would be continually increasing, were it not from the fact that the leaves of trees and plants take in carbon dioxide, assimilate the carbon and expel oxygen.

The constant composition of the atmosphere is maintained through processes of diffusion, and the action of winds in keeping the gases thoroughly mixed.

Ventilation. In rooms, public halls, theatres, mines and factories, the air rich in carbon dioxide cannot be removed by wind, and artificial methods have to be adopted, known as ventilation.

Now, although carbon dioxide is heavier than air under normal conditions, the mixture of air and carbon dioxide is lighter, when warm, than cold air, and in consequence tends to collect in the upper parts of the room.

To ventilate a room it is therefore necessary to remove the air from the upper regions, and to inject fresh air at lower levels. The air may be removed from the room by means of hoods in which a partial vacuum is produced, or by means of electric fans placed in apertures near to the roof. In some systems of ventilation the air is forced into rooms by means of fans, and in certain cases is filtered by passing through felt to remove dust, etc.

An atmosphere containing a high percentage of carbon dioxide is very detrimental to health, and the Factory Acts stipulate that the air in factories must not contain 20 parts or over of carbon dioxide in 10,000 parts by volume of air.

Haldane's apparatus for the estimation of carbon dioxide in the air of factories and workshops. The measuring burette *A* (Fig. 55) is of about 20 c.c. capacity, the lower narrow capillary portion only being graduated, each division of the scale representing $\frac{1}{10000}$ of the total volume of *A*. The burette communicates through the three-way tap, *B*, with the outer atmosphere and also with the absorption pipette, *C*, containing a 15 per cent. solution of caustic potash. The capillary portion of *A* is also in communication with the pressure bulb, *H*, containing mercury, and the bulb is hooked on to a rack and pinion for varying the pressure. The potash pipette, *C*, communicates through the T-tube with the tube, *D*, and the levelling bulb, *E*. The tube *D* is in communication through the three-way tap, *F*, with the control bulb, *G*, whilst at the same time *G* may be put into communication with the outer atmosphere through *F*. The bulbs, *A* and *G*, are placed in a water jacket, through which air is blown to secure a uniform temperature.

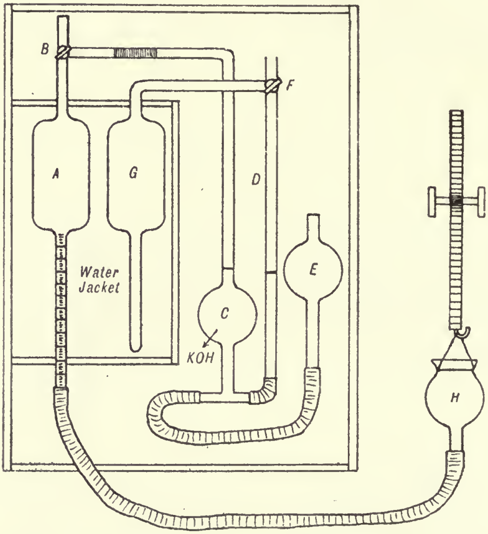


Fig. 55. Haldane's apparatus for estimation of CO_2 in air of factories, etc.

The working of the apparatus is as follows: The bulb, *H*, is raised to expel all air from the burette, *A*, through *B* to the atmosphere, and the sample of air to be tested is drawn in by lowering *H*, until the mercury is approximately on the zero of the scale. The tap *B* is turned to put *A* and *C* into communication; the tap *F* is turned to put *G* into communication with the outside atmosphere and then turned to put *G* and *D* into communication, the height of *E* being then adjusted until the potash in the tube *D* is on a definite mark. The potash in the bulb *C* is arranged on the mark by raising or lowering the bulb *H* and the reading on the capillary tube of *A* is taken. The air is then passed from *A* to *C* by raising the bulb *H*, and the gas is drawn backwards and forwards once or twice. The readings are then again taken by repeating the adjustments as before, (1) by adjusting the level in *D* by means of *E*, (2) by adjusting the level of potash in *C* by means of *H* and taking the reading on the scale of *A*.

An estimation may be made in about 5 minutes and is accurate to 1 part of CO_2 in 20,000 parts by volume of air.

Water vapour in air.

If a perfectly dry flask is taken and ice-cold water poured into it, the outside of the flask very soon becomes covered with a film, due to the condensation of water vapour from the atmosphere.

The presence of water vapour in air may be further proved by the deliquescence of good drying reagents, such as phosphorus pentoxide, or anhydrous calcium chloride, and further by the increase in weight of the drying reagents when exposed to a moist atmosphere. The amount of water vapour in the atmosphere varies considerably according to the conditions of weather and temperature. In warm weather the atmosphere is capable of holding much more water vapour than in cold weather.

This has been already shown, see p. 20, by the increase in the maximum pressure of water vapour by increase in temperature of the space containing the water vapour.

Estimation of water vapour in air. To estimate the amount of water vapour present in the air, the method shown in Fig. 54 may be used, the drying tube being weighed before and after the experiment, and from the volume of air passed through the apparatus, the percentage of water vapour may be calculated, either by weight or by volume. This result gives the actual or absolute amount of water in the atmosphere, but since the atmosphere is capable of holding various amounts according to the temperature it does not give the degree of saturation.

Now the feeling of "wetness" or, in the terms more commonly used, the **humidity of the atmosphere**, is dependent on the degree of saturation, that is to say on the amount of water vapour that it can still absorb. If the air at a particular temperature is almost saturated, then, by a very slight lowering of the temperature, it will become saturated and deposit moisture, but if the air at this same temperature is not near the saturation point then a considerable lowering of the temperature will be necessary in order to cause the deposition of moisture. The amount of lowering of the temperature required to bring about the deposition of moisture may be made a measure of the degree of saturation, and therefore a measure of the humidity of the atmosphere.

Hygrometers. These instruments are used for finding the temperature, termed the **dew point**, at which the air is saturated by the water vapour contained in it.

In **Dines'** hygrometer ice-cooled water is allowed to flow under a thin black glass plate, which may preferably be of polished silver, or silvered metal, and the temperature of the plate is taken by placing the bulb of a thermometer in the water immediately under it. The top of the plate is carefully dried before the experiment. The water is allowed to flow and as soon as the plate is dimmed by the deposition of "dew," the temperature is read on the thermometer. This temperature is the "dew point."

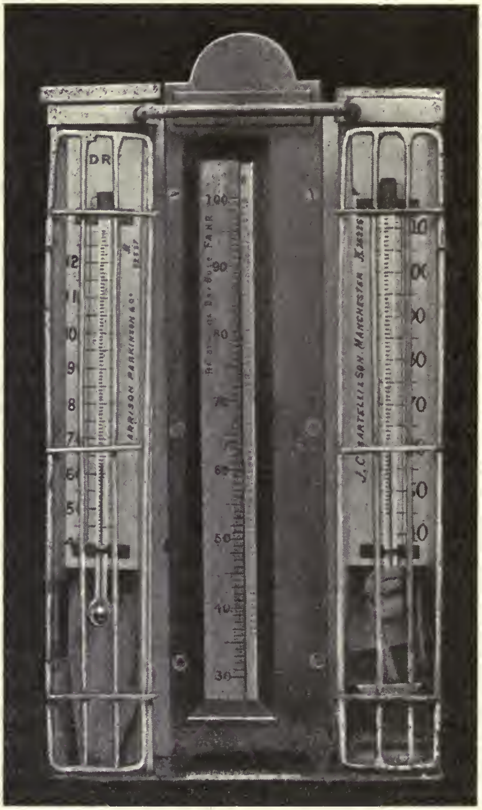


Fig. 56. Wet and dry bulb thermometer, for the determination of the relative humidity of the atmosphere.

The **wet and dry bulb thermometer,** usually employed for determining the humidity of the atmosphere (Fig. 56), measures the capacity of the air to take up water vapour, and the further the temperature of the atmosphere is from the saturation point, the greater will this capacity be. When water passes into vapour heat is absorbed (as shown in a previous chapter), and the faster the water evaporates the more rapidly the temperature will fall. The instrument consists of two thermometers mounted on a stand, and the bulb of one of the thermometers is covered with muslin, which is kept moist by means of a connecting thread or wick dipping into a small vessel containing water.

If the atmosphere is saturated with water vapour, no water will evaporate from the muslin on the thermometer, and there will be no loss of heat; therefore the wet thermometer will register the same temperature as the dry one. If the atmosphere is, however, very dry, that is to say the temperature is a long way removed from the "dew point," the air round the muslin-covered bulb will take up moisture and the water on the muslin will begin to evaporate. This evaporation results in the absorption of heat from surrounding objects, and the temperature of the wet bulb thermometer will fall. In this way the wet bulb thermometer will always show in an unsaturated atmosphere a lower temperature than the dry bulb, and the drier the atmosphere the greater will be the difference between the two readings. When the air is completely saturated with water vapour, the saturation is expressed as 100 per cent., but if the air is not saturated the weight of water actually contained in it is expressed as a percentage of the weight required to saturate it at that temperature, and this percentage is termed the **relative humidity.** Thus, if 100 parts by weight of water are required to saturate the air at the temperature t°C., but the air actually contains 70 parts by weight of water at t° C., the relative humidity is 70 per cent.

There are several ways of obtaining the relative humidity from the readings of hygrometers. The observation of the "dew point" may be used as follows:

$$\text{Temperature} = t^\circ \text{ C.} \qquad \text{Dew point} = t_1^\circ \text{ C.}$$

From tables of vapour pressure (see appendix) the maximum pressures of the water vapour at t° C. and t_1° C. are obtained $=p$ (at t°) and p' (at t_1° C.), then relative humidity

$$= \frac{p' \times 100}{p}.$$

With the wet and dry bulb hygrometer, the relative humidity may be obtained in several ways.

Method 1. The dew point may be calculated approximately from the following formula:

$$\text{Depression of dew point} = t - t_{dp} = f(t - t_w),$$

where $t =$ temp. of dry bulb,

$t_{dp} =$ dew point,

$t_w =$ temp. of wet bulb,

$f =$ varying factor depending on temperature of dry bulb.

The factors are tabulated below from $-10°$ C. to $30°$ C., the figures on the left-hand vertical column and on the top line representing temperatures of dry bulb; thus the factors on the first line are for $-10°$ C., $-10°+1=-9°$ C., $-8°$ C., and so on, and on the second line the factors are given for $0°$ C., $1°$ C., $2°$ C., and so on to $9°$ C.

Dry bulb temp. t	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
−10°	8·76	8·73	8·55	8·26	7·82	7·28	6·62	5·77	4·92	4·04
0°	3·32	2·81	2·54	2·39	2·31	2·26	2·21	2·17	2·13	2·10
+10°	2·06	2·02	1·99	1·95	1·92	1·89	1·87	1·85	1·83	1·81
20°	1·79	1·77	1·75	1·74	1·72	1·70	1·69	1·68	1·67	1·66
30°	1·65	1·64	1·63	1·62	1·61	1·60	1·59	1·58	1·57	1·56

These are Glaisher's factors but only give approximate results.

Example. Reading dry bulb $=15°$ C.

„ wet bulb $=11°$ C.

$$\text{Depress. of dew point} = f(t-t_w)$$
$$= 1{\cdot}89(15-11) = 7{\cdot}56°.$$
$$\text{Dew point} = 15° - 7{\cdot}6° = 7{\cdot}4°\text{ C.}$$

Maximum vap. press. at $7{\cdot}4°$ C. $=7{\cdot}7$ mm.

„ „ „ „ $15°$ C. $=12{\cdot}7$ mm.

$$\text{Relative humidity} = \frac{7{\cdot}7 \times 100}{12{\cdot}7} = \mathbf{60{\cdot}6\ per\ cent.}$$

Tables of maximum pressures of water vapour for the Fahrenheit and Centigrade scales are given in the appendix (Tables 2 and 3).

Method 2. In Table 4 given in the appendix, the temperatures of dry bulb $=t°$ C., the differences, $D°$, between the two bulbs are represented by the figures on the top line, and the figures given are vapour pressures in mm. of mercury at different temperatures with various differences between the two bulbs.

Tables are given for both Centigrade and Fahrenheit scales (see appendix, Tables 4 and 5), as in textile factories the Fahrenheit wet and dry bulb thermometer is generally used. In the Fahrenheit table, the vapour tension in mm. of mercury is given every 2° F. of temperature dry bulb, for each 1° F. difference, but the mean of adjacent figures may be taken to obtain pressures for intermediate readings.

The tables are used as follows:

$t°$ = temperature of dry bulb,

$D°$ = Difference between two bulbs,

then relative humidity

$$= \frac{\text{amount of water vapour actually present at } t°\text{ C.} \times 100}{\text{amount of water vapour required to saturate at } t°\text{ C.}}$$
$$= \frac{\text{vapour press. at } t° \text{ (difference of } D°) \times 100}{\text{vapour press. at } t° \text{ (difference of } 0°\text{ C.)}}.$$

Example: $t = 15^\circ$ C., $D = 4^\circ$.

$$\text{Relative humidity} = \frac{7{\cdot}8 \times 100}{12{\cdot}7} = \mathbf{61{\cdot}4 \text{ per cent.}}$$

Method 3. The degree of saturation or relative humidity may be read off directly on the curves shown (Fig. 57), for the Fahrenheit scale, which is in most common use for textile work. A similar curve may be constructed for the Centigrade scale. Thus the percentage may be read as follows :

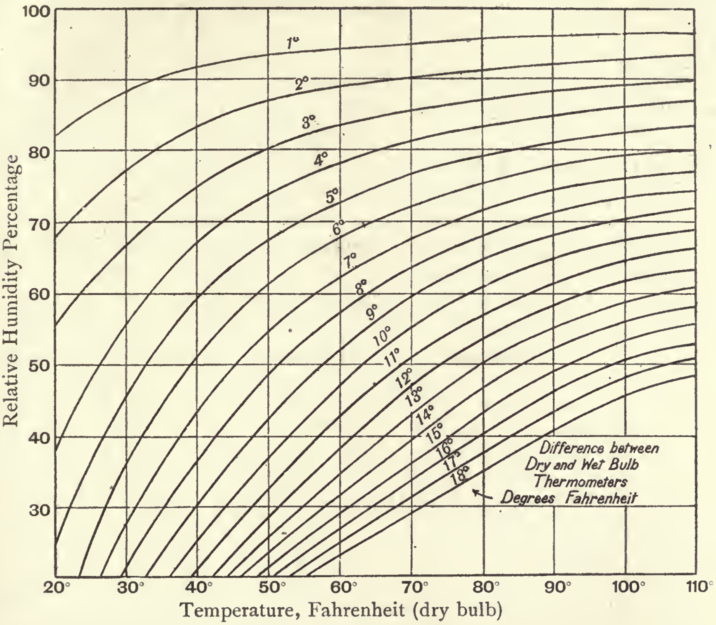


Fig. 57. Chart showing percentage of relative humidity from temperature of air (dry bulb) and difference in temperature between dry and wet bulb thermometers.

Dry bulb reading	Difference between wet and dry bulb readings	Relative humidity or percentage of saturation
60° F.	0° F.	100 %
	1° F.	95 %
	2° F.	89 %
	3° F.	84 %
	4° F.	78 %
	5° F.	73 %
	6° F.	68 %
	7° F.	62 %
	8° F.	57 %
	9° F.	52 %

Method 4. For textile work a special instrument is often used, shown in Fig. 56, with a table of figures representing percentages of relative humidity engraved or mounted on a revolving cylinder. The cylinder is revolved by a knob until a number representing the difference in temperature between dry and wet bulbs is exposed at the top of the column. Opposite the dry bulb reading on the scale will be found the percentage of relative humidity.

Conditioning of textile materials. The moisture of the atmosphere has a marked effect on the condition of textile fibres. All fibres when exposed to the atmosphere under normal conditions absorb moisture, the amount depending on (*a*) the kind of material, (*b*) the relative humidity, and (*c*) temperature of the atmosphere.

The terms **regain** and **direct loss** are used to indicate the amounts of water present in various materials, and as the amount of water may vary according to atmospheric conditions, the following quantities have been officially fixed as standard amounts of moisture.

Materials	Regain %	Direct loss %
Scoured wools	16	13·77
Noils	14	12·3
Tops combed with oil	19	15·97
„ „ without oil	18·25	15·43
Twisted yarns	18·25	15·43
Corded woollen yarns	17	14·53
Shoddy yarn	13	14·15
Cotton	8·5	7·1
Silk	11	9·86
Flax and Hemp	12	10·71
Jute	13·75	12·09

The figures for cotton are for unmercerised material. After mercerisation the increased affinity for moisture is very striking and the regain is approximately 12 per cent. for mercerised cotton. In many cases an allowance of 11 per cent. of moisture is allowed for in commercial transactions in mercerised cotton.

The term **regain**, as used here, means that by exposing 100 parts by weight of any of the above in an absolutely dry condition to the atmosphere, under normal or average conditions, the material will regain the amount of moisture indicated in the table.

The term **direct loss** is used to indicate the amount of moisture lost by drying 100 parts by weight of the material in proper or correct condition.

It is of interest to note that 2 grams of wool will re-absorb as much moisture in converting it from the "bone-dry" condition, to the official standard of regain, as is contained in 1 cu. ft. of air saturated with water vapour at 60° F.

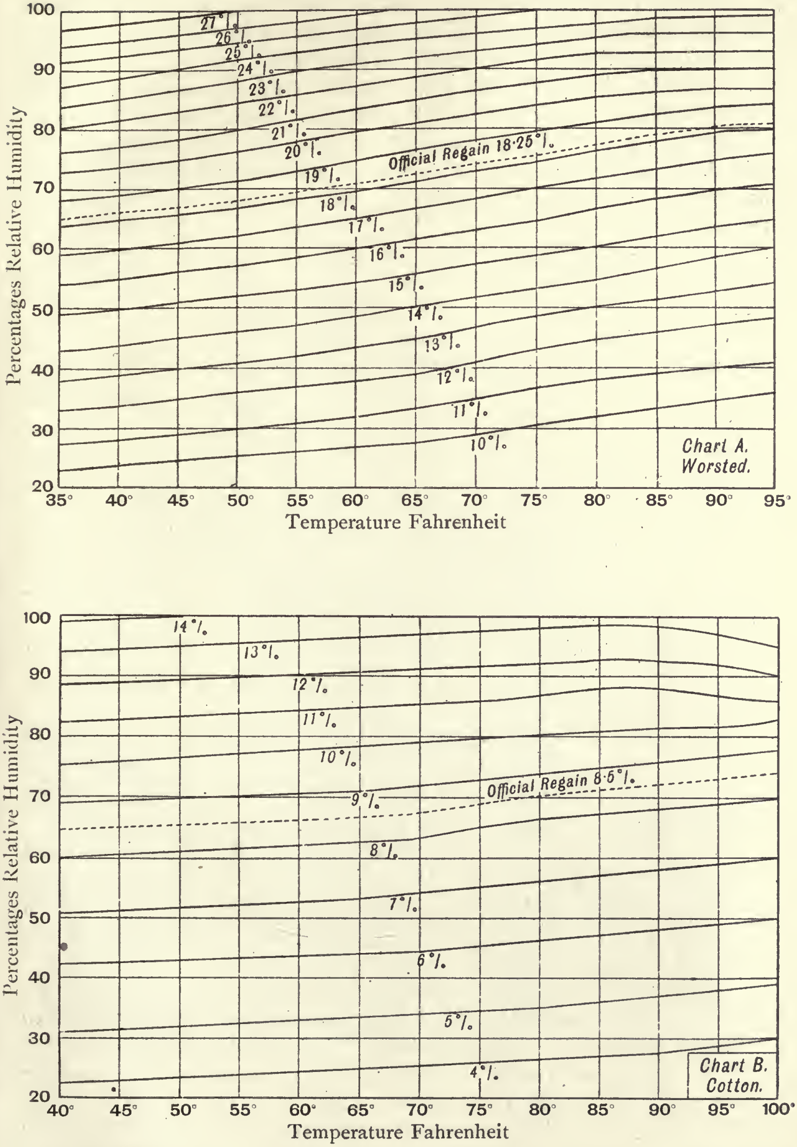


Fig. 58. Worsted and cotton regain lines. Showing percentages of regain of moisture in worsted and cotton for various conditions of temperature and relative humidity. Chart *A*—worsted; Chart *B*—cotton. The standard regain in each case is shown by the dotted line.

This shows how important it is in the conditioning of textile materials to bring a sufficient quantity of air into contact with the material if the maximum quantity of moisture is to be absorbed.

It should be carefully noted that if moist wool or cotton is put into a dry atmosphere, it will lose moisture, or if dry wool is put into a moist atmosphere it will take up moisture, until in each case a balance is obtained. When this balance is attained, the material is giving up moisture at the same rate as it is absorbing moisture, and the percentage of moisture then remains constant. The percentages may be more or less than are shown by the above table, as the amount of moisture taken up will depend entirely on the relative humidity of the surrounding atmosphere and its temperature.

This is shown in the charts for wool and cotton (Fig. 58), in which the percentages of moisture absorbed under different conditions of relative humidity and temperature are represented by the sloping lines. The lines representing the standard regain for cotton and wool are indicated by dotted lines, and it is interesting to note that these amounts of moisture are obtained in the wool and cotton when the atmospheric conditions are about normal, that is, with a temperature of about 60° F. and approximately 70 per cent. relative humidity. Further, a high percentage of moisture can only be obtained in the material by having a high relative humidity, and as a general rule a greater percentage of moisture is obtained in the materials at lower temperatures than at higher.

Sufficient attention is not paid to these points by manufacturers in conditioning, and often an attempt is made to obtain a high regain under absolutely impossible conditions.

This question is important not only in actual conditioning, but also in regulating the humidity of spinning sheds in order to secure good spinning conditions, and in regulating the humidity of cotton factories, in weaving, etc.

For further information on the subject the reader is referred to articles by one of us in the *Textile Recorder* (see "The humidity of the atmosphere in regard to textiles," North, *Textile Recorder*, Oct., Nov., 1918, Feb., April, 1919).

Determination of condition of wool, etc. In determining the condition of the material, 1 lb. of the wool, yarn, etc., is taken so as to obtain a representative sample. Thus wool would be taken from the outside, intermediate portion, and inside of the bale, and yarn is similarly dealt with so as to obtain an average sample.

The sample is dried in a **conditioning oven** (Fig. 59) which is simply a large form of air oven, heated by special burners, the material being arranged inside a cage suspended from a balance. Weights are added to maintain the balance, and giving the amount of moisture lost by the 1 lb. of material. The temperature of the oven is taken by means of a thermometer, and is maintained fairly constant at 220° F.—230° F., the heating being continued for at least 5 minutes after the material is constant in weight.

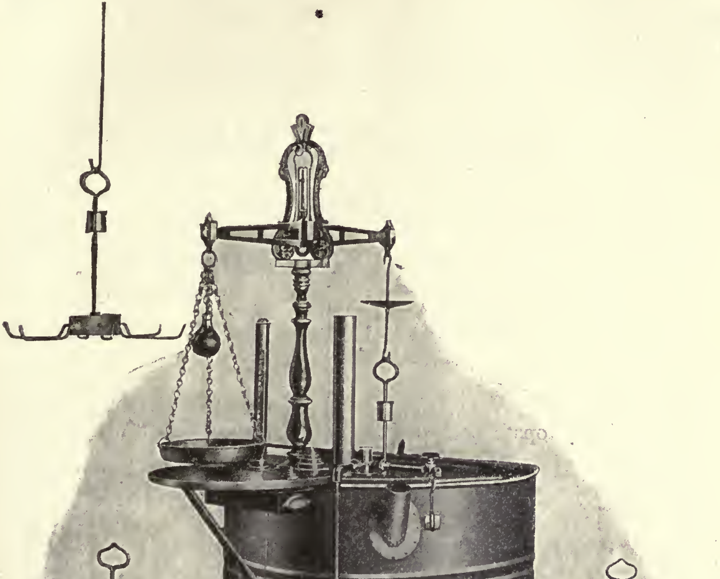


Fig. 59. Conditioning oven. Heal's standard form, reproduced by permission of Messrs Jas. H. Heal, Halifax.

The conditioning oven shown in Fig. 59 is a special form introduced by Messrs J. H. Heal & Co., Halifax, and is a very efficient form, as the drying is done entirely by the circulation of hot air, thus preventing charring of the material, whilst the moisture-laden air is removed ensuring rapid drying of the material.

This method is the official one used in "conditioning houses," where the percentage of moisture is determined and a guarantee or certificate of the condition of the material is given.

The following example will illustrate how the weight of material sold is calculated and invoiced.

10,000 lb. of tops combed in oil are sold in a condition not correct (over conditioned). Tests gave the following results :

1 lb. of material taken (256 drams).

Loss in weight = 2 ozs. 10 drams (42 drams).

Percentage loss or direct loss $= \dfrac{100 \times 42}{256} = 16{\cdot}4$ per cent.

Dry wool in the tops = 83·6 per cent.
100 lb. of tops will produce 83·6 lb. of dry tops.
10,000 lb. „ „ 8360 lb. „ „

In regain :

100 lb. of dry tops become 119 lb. tops in correct condition.

8360 lb. „ „ „ $\dfrac{119 \times 8360}{100} = 9448$ lb. of tops combed with oil in correct condition.

This is the weight invoiced to the buyer.

CHAPTER XVII

COMPOUNDS OF NITROGEN

Ammonia: Ammonium salts: Ammonia as a scouring agent: Oxides and oxy-acids of nitrogen: Nitric acid: Nitre cake: Fixation of atmospheric nitrogen: Nitrates: Nitrogen monoxide: Nitric oxide: Nitrogen peroxide.

Ammonia, NH_3.

If a mixture of three volumes of hydrogen and one volume of nitrogen is submitted for some time to the action of electric sparks, the gases combine together to a certain extent to form ammonia. It is only, however, in very recent years, that the manufacture of ammonia from N and H has been made possible, and this process has already been referred to under the properties of nitrogen (see p. 140).

Most of the ammonia is obtained commercially from the ammonia liquor, collected at the gas works, as a by-product in the manufacture of coal gas. The ammonia is recovered by heating with lime in special stills, and the ammonia converted into ammonium sulphate or chloride by passing into sulphuric or hydrochloric acid respectively, or the gas may be absorbed in water for the preparation of ammonium hydroxide or ammonia solution.

Preparation of ammonia gas. Ammonia is obtained in the laboratory by mixing ammonium chloride with slaked lime, and heating in a dry flask as shown (Fig. 60). The following reaction takes place:

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + 2H_2O$$

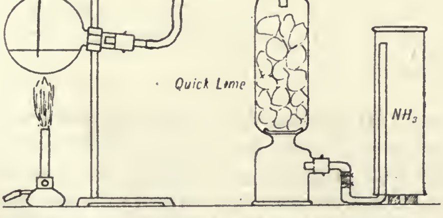


Fig. 60. Preparation of dry ammonia gas.

The gas is dried by passing it through a tower containing lumps of freshly-burnt quick lime, the usual drying reagents, conc. H_2SO_4 and granular $CaCl_2$ used for gases, combining with ammonia. As the gas is lighter than air, it should be passed into the top of the tower, in order to displace the heavier air, and then collected by upward displacement in a gas jar as shown in the figure; as the gas is very soluble in water, it cannot be collected over the ordinary water pneumatic trough but may be collected over mercury.

Properties. Ammonia is a colourless gas with a very powerful pungent odour, and lighter than air; it is moderately easily converted into a liquid, *viz.*, at −37° C., or at ordinary temperatures under 7 atmospheres pressure. The rapid evaporation of liquid ammonia, producing cold, is made use of in refrigerating plants for the manufacture of ice, cold storage, etc.

Ammonia gas is the most soluble of all known gases in water, 1 volume of water at 0° C. dissolving about 1000 volumes of ammonia, or at 15° C., about 850 volumes. The gas and water combine together chemically with the production of ammonium hydroxide, NH_4OH, which acts as a powerful alkali, and ammonia gas is therefore usually stated to possess basic properties, the group **ammonium, NH_4**, known as a **compound radical**, playing the part of an atom of an alkali metal.

$$NH_3 + H_2O \rightarrow NH_4OH$$

This basic property is shown by the affinity for, and combination of the gas with, acids with the formation of salts, similar to the alkali salts, sodium and potassium, thus:

$$\begin{array}{ccc} NH_3 + & HCl & \rightarrow NH_4Cl \\ \text{ammonia} + & \text{hydrochloric acid} & \rightarrow \text{ammonium chloride} \end{array}$$

$$\begin{array}{ccc} 2NH_3 + & H_2SO_4 & \rightarrow (NH_4)_2SO_4 \\ & & \text{or } 2NH_3,\ H_2SO_4 \\ \text{ammonia} + & \text{sulphuric acid} & \rightarrow \text{ammonium sulphate} \end{array}$$

These salts are very important commercial substances and can also be made by mixing ammonium hydroxide with the acid.

$$\begin{array}{l} NH_4OH + HCl \rightarrow NH_4Cl + H_2O \\ 2NH_4OH + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2H_2O \end{array}$$

Ammonia is combustible in air, if heated, or will burn in oxygen at ordinary temperatures with a greenish-yellow flame; if mixed with oxygen it may form an explosive mixture.

Experiments to demonstrate the properties of ammonia.

Solubility in water. A flask, preferably made with a long neck, is filled completely with ammonia gas, tightly corked with a rubber cork, and the latter withdrawn under the surface of water in a trough. The water rushes very violently into the flask, which may easily be driven out of the hand unless gripped tightly during the inrush of water. The alkaline character may be shown simultaneously by adding a few drops of phenol phthalein solution to the water, the liquid then turning violet on entering the flask.

The apparatus shown in Fig. 61 may be used as an alternative method, the upper flask, *A*, being filled with NH_3 and fitted to the cork. By a short blast through the side tube a little water is driven up into the ammonia, thus starting the solution, and producing a partial vacuum. The water rushes in violently, producing a fountain, and the liquid turns violet on entering, if a little phenol phthalein solution is first added to the water.

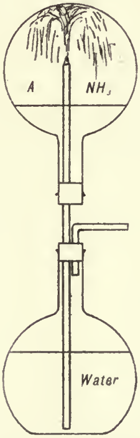


Fig. 61. Showing solubility of ammonia gas in water.

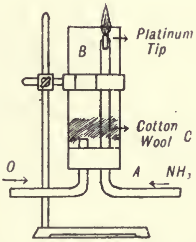


Fig. 62. Combustion of ammonia gas in oxygen.

Combustibility in oxygen. Ammonia is passed slowly through the jet tube, *A*, Fig. 62, which is surrounded by a wide tube, *B*, and the latter is fed with oxygen, the cotton wool at *C* serving to diffuse the gas throughout the wide tube. When the oxygen surrounds the jet tube, *A*, the ammonia may be lit and burns with a greenish-yellow flame.

Combination with acids with production of ammonium salts. Two similar gas jars are filled, one with ammonia gas and the other with hydrochloric acid gas; the latter, which is heavier than air, may be produced by heating concentrated hydrochloric acid. The two jars are brought mouth to mouth, so that the gases may become mixed; dense white fumes of ammonium chloride, settling out as a white solid, are produced.

Scouring properties of ammonia. Ammonia is often used for the removal of grease from fibres, especially fibres that have been woven into cloth, and, in conjunction with soap, it is frequently employed for scouring purposes generally.

Its value as a scouring agent is due to its alkaline property, and power of combining with acids with the formation of soluble salts ; thus, grease, fats, etc., are decomposed, the acid present in the fat or oil combining with the ammonia with the production of soluble ammonium compounds, which themselves have often a value as scouring agents.

Oxygen compounds of nitrogen.

There are three oxy-acids and five oxides of nitrogen known, *viz.*:

Oxy-acids: Nitric acid—HNO_3,
Nitrous acid—HNO_2,
Hyponitrous acid—HNO.

Oxides: Nitrous oxide—N_2O,
Nitric oxide—NO,
Nitrogen trioxide or Nitrous anhydride—N_2O_3,
Nitrogen tetroxide or Nitric peroxide—N_2O_4 or NO_2,
Nitrogen pentoxide or Nitric anhydride—N_2O_5.

Of these compounds, the most important one is nitric acid, the other oxides and acids being mostly of little importance to the textile student, except in so far as they give rise to, or are formed from nitric acid.

Nitric acid, HNO_3.

Preparation. Nitric acid is prepared by the action of strong sulphuric acid on potassium or sodium nitrate. All nitrates, when treated with concentrated sulphuric acid, behave similarly, though sodium nitrate is commonly used on a large scale, because of its cheapness, through large natural supplies being available. Further, the molecular weight of $NaNO_3$ being less than that of KNO_3, it follows that to obtain the same weights of HNO_3, a less quantity of $NaNO_3$ will be required than of KNO_3.

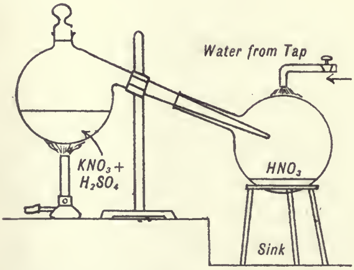


Fig. 63. Preparation of nitric acid.

In the laboratory, potassium nitrate is used, and is heated with conc. H_2SO_4 in a retort, as shown in Fig. 63, the nitric acid vapour being condensed in the cooled receiver. The following reaction takes place :

$$KNO_3+H_2SO_4 \rightarrow HNO_3+KHSO_4$$

If a further quantity of the nitrate is added and the substances heated to a red heat, the following further reaction may be obtained :

$$KNO_3+KHSO_4 \rightarrow K_2SO_4+HNO_3$$

At a red heat a considerable amount of the nitric acid is decomposed, and even at lower temperatures when nitric acid is distilled a small quantity is split up, thus:

$$2HNO_3 \rightarrow H_2O + N_2O_4 + O$$

Manufacture of nitric acid. On the manufacturing scale nitric acid is obtained from sodium nitrate and concentrated sulphuric acid, which are heated in cast iron retorts, or in retorts constructed of acid-resisting metal, such as "Narki" metal, the nitric acid being condensed in pipes and towers of acid-resisting material or metal or silica ware and collected in similar jars. The nitre cake is run off in a molten condition from the retort at the end of the action.

The following actions take place:

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$$
$$NaNO_3 + NaHSO_4 \rightarrow Na_2SO_4 + HNO_3$$

Nitre cake. In the manufacturing process a balance is struck between the above reactions, the object being to bring about the maximum production of nitric acid and normal sodium sulphate, with the minimum decomposition of nitric acid as described above. The result, in the manufacturing process, is that the residue, known as nitre cake, consists of a mixture of the acid salt, $NaHSO_4$ (Na_2SO_4, H_2SO_4), and the normal salt, Na_2SO_4, containing from 24 to 32 per cent. of sulphuric acid, as the production of nitric acid from the acid salt and the nitrate is not carried to its extreme limit. Further, sodium sulphate alone, having a higher melting point, is liable to set hard in the retort and is difficult to remove.

Nitre cake has been largely used in recent years as a source of sulphuric acid, and has been suggested for carbonising in textile operations, an operation which will be referred to more in detail under the uses of sulphuric acid.

Fixation of atmospheric nitrogen and production of nitric acid. There are several methods in use for the production of nitric acid from atmospheric nitrogen, and a great number of patents have been taken out for various types of electric arc furnaces for this purpose. The following may be considered to be typical of these. An electric arc is produced between water-cooled electrodes in a powerful magnetic field, the effect of the latter being to spread the arc in the form of a large hot disc of flame, known as the "electric sun," or the arc may be spread or whirled by a blast of air. Air, or a mixture of nitrogen and oxygen, is fed into contact with this flame, the gases being afterwards drawn off rapidly and cooled, generally by mixing cool air with the gas, so as to prevent dissociation of the oxides of nitrogen (nitric oxide), whilst at the same time forming nitrogen peroxide.

The nitrogen peroxide is absorbed in towers by milk of lime forming calcium nitrate, the following actions taking place:

$$N_2 + O_2 \rightarrow 2NO, \qquad 2NO + O_2 \rightarrow N_2O_4$$
$$2N_2O_4 + 2Ca(OH)_2 \rightarrow Ca(NO_3)_2 + Ca(NO_2)_2 + 2H_2O$$

The Birkeland-Eyde electric furnace. The arc is produced between water-cooled copper electrodes, Fig. 64, and this is spread by the powerful electro-magnets, *A*, *B*, into a disc of flame 8 ft. in diameter in the arc chamber, *C*. The air enters at the bottom and passes in the direction of the arrows through the heat-resisting material forming the body of the chamber, *C*, into contact with the arc. The nitric oxide passing away from the centre of the arc disc comes into contact with cooler air, entering the disc near its circumference, and the NO_2 passes out as shown by the arrows. At Notodden, in Norway, 32 such furnaces taking current up to 5500 volts are in use, and at Saaheim, in Germany, 8 furnaces at 11,000 volts.

This form is only typical of several other forms in use on the continent, a full description of which may be obtained from *Soc. Chem. Ind.* 1915, p. 113, in a paper by Kilburn-Scott.

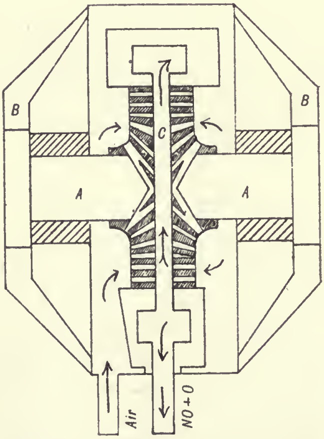


Fig. 64. Birkeland-Eyde furnace for fixation of atmospheric nitrogen.

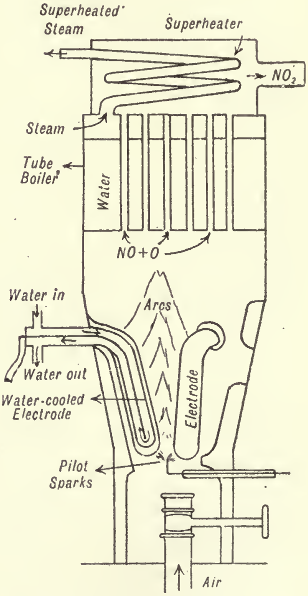


Fig. 65. Kilburn-Scott three-phase furnace for fixation of nitrogen.

Kilburn-Scott electric furnace. Kilburn-Scott has devised an electric furnace for the fixation of atmospheric N, which is shown in section in Fig. 65, the special advantage being that three-phase current may be used. Three arc flames are thus produced in one furnace, and these are blown by the air current into one combined conical flame. The flames are kindled by the pilot sparks shown below the water-cooled electrodes. The hot gases passing away are cooled by the tube boiler, whilst at the same time producing steam and superheating it. The steam can be used for the production of electric energy. It has the advantages of being less in first cost, attendance cost, and maintenance of arc, having also less brickwork, ironwork, foundations, etc., and has only three electrodes instead of six as in three single-phase furnaces. Kilburn-Scott suggests using a mixture of equal parts of N and O, which increases the yield 20 per cent.

Properties. Pure nitric acid is a colourless liquid, sp. gr. 1·53, boiling at 86° C., but decomposing slowly on distillation, thus :

$$2HNO_3 \rightarrow H_2O + N_2O_4 + O$$

The distilling liquid gradually becomes weaker, the boiling point also rising, until it has a sp. gr. 1·414, and a B.P. 120° C.; from this point it distils with a constant boiling point and constant composition, containing 68 per cent. HNO_3, 32 per cent. H_2O; this is the ordinary concentrated nitric acid. The colour of the acid is often yellowish or yellowish-brown from the nitrogen tetroxide, liberated as described above, dissolving in the acid, and in warmer weather, particularly by exposure to light, the acid gradually changes in colour through a slow decomposition of this character. The dissolved N_2O_4 may be expelled, thus rendering the acid colourless, by blowing air through the liquid. **Fuming nitric acid** consists of nitric acid with nitrogen tetroxide in solution and may be obtained by distilling nitric acid with starch.

Oxidising character of nitric acid. The acid is a powerful oxidising agent, owing to the ease with which it liberates oxygen.

The liberation of oxygen may be shown by the experiment illustrated in Fig. 66, concentrated nitric acid being dropped into the bowl of the pipe, and, passing slowly through the red-hot stem, is decomposed. Each drop of acid forms a plug preventing the escape of gas from the bowl, and if the stem is arranged so that the point is not more than ½ inch under the surface of the water, the oxygen may be readily collected.

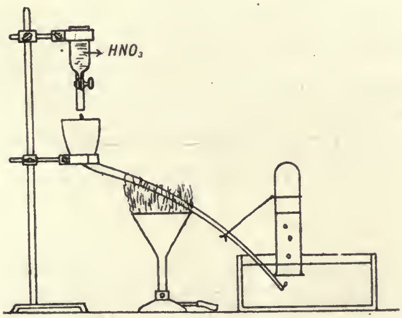


Fig. 66. Decomposition of nitric acid at a red heat.

The oxidising power of the acid may also be shown by pouring it slowly on to powdered charcoal or sawdust heated in a porcelain dish, the temperature of the charcoal increasing, so that it glows red-hot, or it even burns with the production of a shower of sparks. Ferrous compounds, if heated with nitric acid in the presence of a free acid, are readily oxidised to ferric compounds, thus:

$$2FeCl_2 + 2HCl + O \rightarrow 2FeCl_3 + H_2O$$

The blue colour of indigo is discharged by concentrated nitric acid, and this change to the yellow compound which is formed is one of oxidation.

Most of the common metals are readily attacked by nitric acid, and these actions may be considered as oxidation processes, although the metals are mostly converted into metallic nitrates. The metal, however, is first oxidised, though in the presence of free acid the basic oxide cannot exist, and the nitrate of the metal is formed which passes into solution. The nitric acid commonly yields oxygen under these conditions according to one or other of the following equations, though under special conditions other oxides of nitrogen may be liberated:

$$2HNO_3 \rightarrow 2NO + H_2O + 3O$$
$$2HNO_3 \rightarrow N_2O_4 + H_2O + O$$

In the cases of tin and antimony insoluble oxides of the metals are formed, whilst in the case of gold, platinum, and the so-called **noble metals,** the acid has no action upon them.

Special metals, or alloys, mostly ferro-silicons, are now made which are not attacked by ordinary concentrated nitric acid; **tantiron, narki metal,** etc., are such examples, and are finding useful applications in the industries.

From its action on most metals the acid is commonly known commercially as "aqua fortis" ("strong water").

Aqua regia ("royal water"), which is a mixture of $3HCl + HNO_3$ (concentrated acids), will readily dissolve gold, platinum, etc., but forms chlorides of the metals from the action of nascent chlorine thus:

$$3HCl + HNO_3 \rightarrow \underset{\text{nitrosyl chloride}}{NOCl} + 2H_2O + \underset{\text{nascent}}{2Cl}$$

Nitrates. The nitrates are also good oxidising agents, potassium nitrate (saltpetre or nitre), KNO_3, being used for this purpose as a constituent of gunpowder, which contains in addition oxidisable substances such as carbon and sulphur.

When the alkali nitrates (K, Na) are heated, they yield **nitrites** and give up oxygen, thus:

$$NaNO_3 \rightarrow NaNO_2 + O$$

Sodium nitrite, which is largely used in manufacturing organic compounds, may be prepared in this way or preferably by heating $NaNO_3$ with metallic lead:

$$NaNO_3 + Pb \rightarrow PbO + NaNO_2$$

Ammonium nitrate breaks up on heating into nitrous oxide and water, thus:

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

All other nitrates, commonly named the nitrates of the heavy metals, give the basic oxide on heating, thus:

$$Pb(NO_3)_2 \rightarrow PbO + N_2O_4 + O$$

except manganese which gives the dioxide, thus:

$$Mn(NO_3)_2 \rightarrow MnO_2 + N_2O_4$$

Sodium nitrate. The salt is principally obtained from the deposits of "Chili saltpetre," $NaNO_3$, by solution and crystallisation of the mineral substance. The salt is largely used as a source of nitric acid, for the production of potassium nitrate, as an oxidising agent, and for the production of sodium nitrite, which is largely employed in the manufacture of dyestuffs.

Potassium nitrate. This salt is obtained principally by crystallising a mixture of potassium chloride (obtained from the Stassfurt deposits in Germany), and sodium nitrate ("Chili saltpetre").

It is largely used as an oxidising agent, for the production of potassium nitrite, and in the manufacture of gunpowder.

Ferrous and ferric nitrates. These were at one time used for the production of colours, *e.g.*, "Prussian blue," on wool but are now rarely used. The so-called commercial **nitrate of iron** is a basic ferric sulphate and will be referred to again under sulphuric acid and sulphates (see p. 195).

Silver nitrate. Silver nitrate is produced by the action of hot moderately concentrated nitric acid on metallic silver. It is used with ammonia and gum in the preparation of marking inks.

Stannous nitrate, $Sn(NO_3)_2$, is obtained in solution by dissolving 1 part of grain bar tin in 8 parts of nitric acid (32° Tw.), but is only known in the form of an unstable solution. It has been used in the production of cochineal scarlets under the names of "scarlet spirits," "bowl spirits," etc.

Oxides of nitrogen.

Nitric oxide, NO. Nitric oxide may be obtained by the action of nitric acid (1 volume acid, 1 volume water) on copper turnings in an apparatus similar to that used for the preparation of hydrogen. The brown fumes, first produced, are formed by the action of nitric oxide on the oxygen of the air, and will dissolve in water, but the gas should be allowed to escape until the nitric oxide in the generating bottle is colourless. It may then be collected in gas jars over the pneumatic trough.

$$3Cu + 8HNO_3 \rightarrow 2NO + 3Cu(NO_3)_2 + 4H_2O$$

Properties. Nitric oxide is a colourless gas, combining with oxygen and forming nitrogen tetroxide, N_2O_4, immediately it comes into contact with air; consequently the odour and taste of the gas are unknown. As the N_2O_4 fumes are very suffocating, they should not be inhaled. Nitric oxide does not readily support combustion, though a piece of brightly burning phosphorus will continue to burn brightly, forming phosphorus pentoxide and nitrogen.

$$10NO + P_4 \rightarrow P_4O_{10} + 5N_2$$

Nitric oxide is readily absorbed by a strong solution of ferrous sulphate, forming an unstable brown compound, $2FeSO_4$, NO. This compound readily decomposes on heating the solution. It is formed in the "brown ring" test for a nitrate.

Brown ring test for a nitrate. The nitrate and a moderate excess of ferrous sulphate are dissolved in water, the liquid filtered, if necessary, cooled, and concentrated sulphuric acid is carefully poured down the side of the tube, so as to form a heavier layer at the bottom of the liquid; a brown ring is formed where the two liquids meet, if a nitrate is present. The brown colour will disappear on shaking or on heating the liquid.

Nitrous oxide or nitrogen monoxide ("laughing gas"), N_2O. Preparation. Fused ammonium nitrate is heated in an apparatus similar to that used for the preparation of oxygen, and the evolved gas collected over a pneumatic trough containing hot water.

$$NH_4NO_3 \rightarrow N_2O + 2H_2O$$

It is the gas used by dentists, and for this purpose must be carefully purified, by passing through solutions of caustic soda and ferrous sulphate, to absorb impurities of chlorine and nitric oxide.

Properties. Nitrous oxide is a colourless gas, with a faint smell and a slight sweetish taste. If breathed in considerable quantities, it produces unconsciousness which quickly passes, and it is therefore used as an anæsthetic in dental operations.

It is a good supporter of combustion, will relight a glowing splinter of wood, and brightly burning sulphur, phosphorus, etc., will burn very brilliantly in nitrous oxide, the following actions taking place:

$$S + 2N_2O \rightarrow SO_2 + 2N_2$$
$$P_4 + 10N_2O \rightarrow P_4O_{10} + 10N_2$$

It may be distinguished from oxygen (1) by its solubility in water, 1 volume of water dissolving about 1 volume of N_2O, (2) by the action of nitric oxide, NO, on oxygen, producing brown fumes of N_2O_4, whereas nitrous and nitric oxides have no action on each other.

Nitrogen tetroxide or peroxide, N_2O_4 or NO_2. Preparation. Dry powdered lead nitrate is heated in a retort, and the evolved gas is passed into a U-tube immersed in a freezing mixture of ice and salt.

$$2Pb(NO_3)_2 \rightarrow 2PbO + N_2O_4 + O$$

Properties. At low temperatures it forms a colourless solid, melting at − 9° C. to a colourless liquid, but changing in colour, as the liquid rises in temperature, from a greenish to a yellowish and orange tint. The liquid boils at 22° C. forming a reddish-brown gas which darkens on heating, until at 140° C. it is opaque and almost black.

These changes in colour are accompanied by corresponding changes in vapour density as shown in the following table:

Temperature	Vapour density $H=1$	Percentage of NO_2 molecules
27° C.	38	20
60° C.	30	50
100° C.	25	80
140° C.	23	100

As indicated in the last column of the above table, the changes are due to the gradual breaking up of the complex N_2O_4 molecules into NO_2 molecules, the change being complete at 140° C. The reverse changes, in colour, density, and composition of the molecules, take place on cooling the gas, the action being represented

$$N_2O_4 \rightleftarrows 2NO_2$$

At about 500° C., the gas becomes colourless, due to the following action:

$$2NO_2 \rightleftarrows 2NO + O_2$$

Dissociation. Such actions, which are quite distinct from decomposition, are known as dissociation, and this action may thus be defined:

Dissociation is the breaking up of a complex molecule into simpler molecules by the effect of heat or change of pressure, the original complex molecule being formed when the original conditions are again restored.

CHAPTER XVIII

CHLORINE AND ITS COMPOUNDS

HYDROCHLORIC ACID: MANUFACTURE: CHLORIDES: CHLORINE: MANUFACTURING PROCESSES: BLEACHING AND BLEACHING MATERIALS: BLEACHING POWDER IN THE BLEACHING OF COTTON: OXIDES AND OXY-ACIDS OF CHLORINE: ELECTROLYTIC BLEACHING LIQUORS.

Hydrochloric acid.

Preparation. If a mixture of equal volumes of hydrogen and chlorine is passed in the dark into a thin glass bulb, no change takes place, but if the bulb containing the gases is brought into the direct rays of the sun or an arc light, the two gases combine with explosion and the glass bulb is shattered.

Again, if a tube is filled with hydrogen and chlorine in the proportions given above, and then exposed for some time to diffused daylight, combination takes place slowly; the green colour of the chlorine disappears, and the whole of the remaining gas is soluble in water. The hydrogen and chlorine have thus combined to give another gas, named hydrochloric acid, which is different in properties from either of the gases, hydrogen and chlorine.

Hydrochloric acid is, however, more conveniently prepared in the laboratory in the following manner.

An eight-ounce flask is fitted with a 2-hole rubber stopper, a thistle funnel passing nearly to the bottom of the flask, and a glass delivery tube, as shown in Fig. 67. Sodium chloride (common salt or rock salt) is placed in the flask and strong sulphuric acid poured down the thistle funnel. Hydrochloric acid gas is immediately evolved, but the evolution is much more vigorous, if the flask is slightly warmed. As the gas is a heavy one, it can be conveniently collected by downward displacement, but cannot be collected over water as it is extremely soluble. The following action takes place:

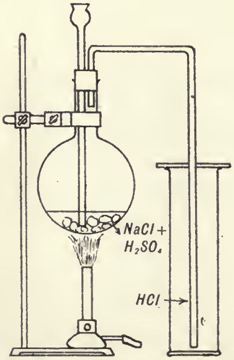


Fig. 67. Preparation of hydrochloric acid gas.

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$$

Manufacture. On the manufacturing scale hydrochloric acid, known commercially as "muriatic acid," is made by a similar process, although the apparatus used is very different.

Sodium chloride and strong sulphuric acid are mixed in a shallow iron pan, which is heated by means of a fire placed underneath, and hydrochloric acid is evolved, with the formation of sodium hydrogen sulphate. When this reaction is complete the mixture is raked on to the hearth of a **reverberatory furnace** shown in Fig. 68. The mixture now comes into direct contact with the hot gases and flames from the fire, and the temperature is raised considerably, the following further action taking place :

$$NaCl + NaHSO_4 \rightarrow Na_2SO_4 + HCl$$

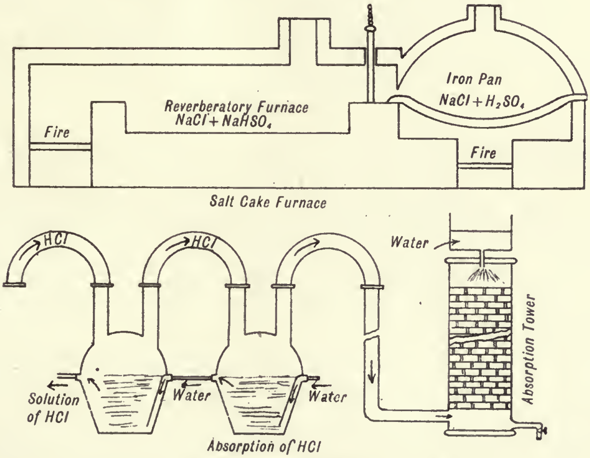


Fig. 68. Manufacture of hydrochloric acid.

The hydrochloric acid is led off through pipes from the pan and the furnace, and passed up towers containing coke or acid-resisting material over which a slow stream of water is falling. The hydrochloric acid dissolves in the water and a concentrated solution is obtained.

In more modern forms of apparatus, the gas is first passed through earthenware bottles over a counter-current of water, *i.e.*, flowing in the opposite direction from one bottle to the next in the series, and the gas is finally passed up a short absorption tower through which water is falling to complete the solution of the HCl, as shown in the lower part of Fig. 68.

Properties. Hydrochloric acid is a colourless, heavy gas, which fumes strongly in moist air. It is extremely soluble in water, one volume of water at 15° C. dissolving 450 volumes of hydrochloric acid gas. This solution contains 43 per cent. of hydrochloric acid and has a specific gravity of 1·2. If the solution is distilled it gradually becomes weaker, until finally a distillate of constant composition is obtained. On the other hand, if a weak solution of hydrochloric acid is distilled, it gradually becomes stronger until again a distillate of the same constant composition is obtained. This acid of constant composition contains 20·24 per cent. hydrochloric acid at normal pressure, and affords a means of obtaining a solution of hydrochloric acid of known strength ; it has a specific gravity of 1·1 and a constant B.P. of 110° C.

At the ordinary temperature hydrochloric acid gas is converted into a liquid by submitting it to a pressure of 40 atmospheres; and the liquid so obtained has no action on metals.

Hydrochloric acid gas, or a solution of the gas in water, reddens blue litmus, neutralises alkalis and acts on many metals, such as zinc, iron, nickel, magnesium, cadmium, tin, etc., with the evolution of hydrogen and the formation of chlorides of the metals, thus:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$
$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

Chlorides. The following chlorides find many important applications in the textile and allied industries.

Sodium chloride occurs in very large quantities in rock salt and in sea water. In its natural state it is very impure but by recrystallisation it can be obtained almost pure. It is the starting point in the manufacture of nearly all the compounds of sodium, *e.g.*, sodium sulphate, carbonate and hydroxide.

It can be prepared in the laboratory by neutralising sodium hydroxide or carbonate by hydrochloric acid and evaporating to dryness.

Potassium chloride is obtained from the Stassfurt deposits in Germany, chiefly in the form of Sylvine, KCl, or Carnallite, $MgCl_2, KCl, 6H_2O$. It can be prepared in the laboratory in a manner similar to the preparation of sodium chloride, using potassium instead of sodium hydroxide. It is largely used for the manufacture of potassium nitrate.

Ammonium chloride ("Sal ammoniac") is obtained by passing ammonia into hydrochloric acid, the ammonia being prepared by heating ammoniacal gas liquor either alone or with lime.

It is purified by sublimation, and is used in electric batteries, soldering, galvanising and in dyeing and calico printing.

Calcium chloride is obtained as a by-product in many chemical operations and can also be made by the action of hydrochloric acid on limestone or chalk. It is sometimes used as a finishing agent for cotton. It is very hygroscopic and absorbs moisture from the air.

Magnesium chloride occurs in small quantities in sea water and in much larger amounts in the mineral, carnallite. The liquors from the carnallite extraction have a specific gravity of 1·32 and contain about 30 per cent. of magnesium chloride. By concentration, liquor of 50 per cent. may be obtained, and this solution sets to a solid having the following composition:

$MgCl_2$	50 per cent.
$NaCl+KCl$	10 ,,
H_2O	40 ,,

This crude magnesium chloride is used as a **lubricant for the fibres in the spinning** of cotton yarns. Magnesium chloride is also used as a **dressing on cotton and woollen textile fabrics**, giving the material a damp full feel, but it should not be used on cotton which has to be heated afterwards, as the action of heat causes the water in the fabric to attack the magnesium chloride, with the liberation of hydrochloric acid which tenders the fibres. Magnesium chloride crystallises with six molecules of water, and on heating these crystals the magnesium chloride partly reacts with the water with the formation of hydrochloric acid and magnesium oxide, thus:

$$MgCl_2+H_2O \rightarrow MgO+2HCl$$

Solutions of magnesium chloride may be prepared by dissolving magnesium, magnesium oxide, or carbonate, in hydrochloric acid.

Zinc chloride is made by the action of hydrochloric acid on zinc, zinc oxide or zinc carbonate. A solution of this salt in water, containing about 40—50 per cent., $ZnCl_2$, and heated to 80—100° C., will slowly dissolve paper and cotton. If the solution of zinc chloride is evaporated or boiled with zinc oxide (1000 parts $ZnCl_2$, 850 parts H_2O, and 40 parts ZnO) the solution of basic zinc chloride obtained (sp. gr. 1·69—1·70) will dissolve silk, and is sometimes used for the estimation of silk in a mixture of cotton, wool, and silk. Zinc chloride is used as a **softening and weighting agent** in the finishing of cotton materials, for producing crimped effects on woven materials, and in small quantities (5 to 10 parts per 1000) as a preservative for preventing the formation of moulds in **dressings for textile materials.**

Zinc chloride is very hygroscopic and quickly absorbs moisture from the air. It is used as a dehydrating agent in organic work, and in the manufacture of dyestuffs.

Anhydrous aluminium chloride is prepared by the action of hydrochloric acid gas on heated aluminium shavings, or by the action of chlorine on a mixture of aluminium oxide and carbon at a red heat. Solutions of aluminium chloride can be obtained by dissolving aluminium hydroxide in hydrochloric acid.

Aluminium chloride is sometimes used in place of sulphuric acid for **carbonising wool**, the aluminium chloride and water reacting together on heating, with the production of HCl gas which attacks the vegetable matter in the wool. It is also used for preserving timber and in calico printing.

Iron chloride exists in two forms, ferrous and ferric chlorides. Ferrous chloride, $FeCl_2$, is made by passing hydrochloric acid gas over heated iron. Ferric chloride can be prepared by dissolving ferric hydroxide in strong hydrochloric acid.

Tin chloride also exists in two forms, stannous and stannic chlorides, $SnCl_2$ and $SnCl_4$.

Stannous chloride is made by dissolving tin in hydrochloric acid, and crystallising as $SnCl_2, 2H_2O$. It is known under the name of **tin salt** or **tin crystals,** but is also put on the market as **single muriate of tin, 60° Tw.,** and **double muriate of tin, 120° Tw.** The salt is used as a **discharging agent** in calico printing, as a **mordant** in silk dyeing, and in dyeing wool with cochineal.

Stannic chloride is made by the action of chlorine on tin, or by oxidising stannous chloride with chlorine or by a mixture of hydrochloric acid and sodium chlorate, $NaClO_3$.

$$3SnCl_2+6HCl+NaClO_3 \rightarrow 3SnCl_4+3H_2O+NaCl$$

It is used as a mordant in dyeing, giving a very brilliant scarlet with cochineal. It is largely used for weighting silk, and is often added to sizes for cotton warps to prevent decomposition of the sizing material.

At one time it was largely put on the market as **pink salt,** $SnCl_4, 2NH_4Cl$, but the solution, or the solid, $SnCl_4, 5H_2O$ (known as **butter of tin** from its consistency) is now usually sold under the name "pink salt."

Tin spirits contains both stannous and stannic chlorides, with or without HCl, HNO_3 and H_2SO_4, but is now not much used.

Chlorine, Cl, At. Wt. 35·5.

Occurrence. Chlorine occurs in nature combined with other elements in the form of chlorides. The most important of these is sodium chloride, which occurs in large quantities in the form of rock salt. Sodium chloride also occurs in sea water and can be recovered from it by evaporation. The first evaporation is carried out at the ordinary temperature by allowing the sea water to flow over large stacks of twigs, thereby exposing a large surface of the solution to the atmosphere. The concentrated solution is finally evaporated in boilers or vacuum pans to obtain the solid.

Another important source of chlorine is carnallite, from the Stassfurt deposits.

Preparation. Chlorine can be obtained from chlorides by the action of manganese dioxide and dilute sulphuric acid:

$$2NaCl+MnO_2+2H_2SO_4 \rightarrow Na_2SO_4+MnSO_4+Cl_2+2H_2O$$

It can also be prepared by the action of manganese dioxide on concentrated hydrochloric acid:

$$MnO_2+4HCl \rightarrow MnCl_2+Cl_2+2H_2O$$

Other modes of preparation are by the action of dilute hydrochloric or sulphuric acid on bleaching powder, and by the action of concentrated hydrochloric acid on potassium dichromate or permanganate.

The most convenient method for laboratory use is the action of manganese dioxide on concentrated hydrochloric acid. The apparatus used is similar to that employed for the preparation of hydrochloric acid; the manganese dioxide in small lumps is gently heated with hydrochloric acid in the flask and the evolved chlorine is collected by downward displacement.

Manufacture. There are several methods in use for the manufacture of chlorine.

Weldon's process. The chlorine is generated by the action of manganese dioxide in the mineral form, "pyrolusite," on hydrochloric acid in a still, formed of slabs of sandstone, or "flagstones." The resulting liquor contains manganese chloride, with excess of hydrochloric acid, and small quantities of ferric chloride formed from impurities in the pyrolusite. Manganese dioxide is recovered from this liquor by neutralising the acid by the addition of limestone or chalk, which also precipitates the iron and the liquor is allowed to settle. The clear liquid, containing manganese chloride and calcium chloride, is mixed with an excess of milk of lime ($\frac{1}{5}$ more than the theoretical quantity is essential to the success of the process) in a vessel known as the oxidiser, and compressed air is blown through the liquor, forming CaO, MnO_2. A further quantity of liquor and milk of lime are added, and compressed air and steam are blown through the liquid. This precipitates a black mud, $CaO, 2MnO_2$, known as "Weldon's mud," which is separated in settling tanks and used again for the manufacture of chlorine, the slight loss in the process being made up by the addition of further quantities of pyrolusite.

Deacon's process. Deacon's process consists in the oxidation of the hydrogen in hydrochloric acid by the oxygen of the air, with liberation of chlorine. The action is brought about by means of a catalytic agent, usually cupric chloride. Hydrochloric acid gas is mixed by means of a blower with four times its volume of dry air, and the mixture is drawn through iron pipes heated to 500° C. The gas is then passed through the decomposer consisting of a cast iron vessel containing bricks soaked in cupric chloride solution. The excess of hydrochloric acid is removed by passing the gas through water, and the chlorine mixed with nitrogen from the air is usually utilised in the manufacture of bleaching powder.

Chlorine is largely manufactured as a by-product in various **electrolytic processes**, *e.g.*, in the electrolytic manufacture of sodium from fused sodium chloride, and in the manufacture of sodium hydroxide by the electrolysis of brine (see p. 331).

Properties. Chlorine is a greenish-yellow gas, with a pungent, suffocating smell. It is liquefied at $-34°$ C., or at ordinary temperatures by a pressure of six atmospheres. It is heavier than air, and soluble in water, one volume of water at 15° C. dissolving about two and a half volumes of the gas. The solution is known as chlorine water, and strongly resembles the gas in many of its properties, such as colour, odour, bleaching, etc. If exposed to sunlight it slowly decomposes into hydrochloric acid and oxygen, the latter escaping in small bubbles.

$$Cl_2 + H_2O \rightarrow 2HCl + O$$

If cooled to 0° C., a saturated solution of chlorine water forms a solid hydrate, yellow in colour, and of the composition, $Cl_2, 10H_2O$.

Chlorine is extremely active and combines with many elements at ordinary temperatures. Thus, phosphorus takes fire spontaneously in the gas, and gives off white fumes, which consist of a mixture of phosphorus trichloride and pentachloride.

Many metals combine readily with chlorine, and in a finely divided state may take fire spontaneously. Thus, finely powdered antimony when sprinkled into chlorine fires spontaneously forming antimony chloride. Dutch metal (largely copper) takes fire, forming $CuCl_2$, and even gold and platinum, which resist the action of most acids, are slowly attacked.

Chlorine has a great affinity for hydrogen as demonstrated by the experiment described at the beginning of the chapter. The affinity for hydrogen is so great, that chlorine will often combine with the hydrogen of other compounds. Thus, if a piece of filter paper is soaked in turpentine, $C_{10}H_{16}$, and placed in a jar of chlorine, the hydrogen of the turpentine combines with the chlorine with a flash, and large quantities of carbon, in the form of soot, are deposited on the sides of the jar.

Bleaching action. Perfectly dry chlorine has no action on colouring matters, and a piece of dyed cloth, or litmus paper, placed in a jar of dry chlorine retains its colour, but, if moisture is present, the colour is rapidly discharged. The bleaching action is not brought about directly by the chlorine, but by the oxygen liberated from water, thus:

$$Cl_2 + H_2O \rightarrow 2HCl + O$$

The oxygen at the moment of liberation is in the nascent condition, and is thus extremely active, combining with the colouring matters and forming colourless compounds.

For this reason chlorine is used extensively for the bleaching of fibres, especially cotton, and for this purpose is usually derived from bleaching powder.

Bleaching powder ("chloride of lime"). Bleaching powder is obtained by passing chlorine over moderately dry slaked lime. In the manufacture of bleaching powder, slaked lime is prepared by treating quicklime with only a small excess of water when the following action takes place:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

The heat of the reaction is very great and drives off most of the excess of water, and the calcium hydroxide falls into a fine powder (about 2 to 4 per cent. excess of water gives the best bleaching powder in practice). The calcium hydroxide is converted into bleaching powder by spreading the lime in shallow layers on shelves in a closed chamber, and chlorine gas is passed into the chamber in such a manner that it comes into close contact with the whole of the lime. Forms of apparatus have also been devised for the continuous treatment of the lime in horizontal cylinders, the lime being fed in at the top, passing from one cylinder to the next below, and falling out from the bottom one in the finished state. The chlorine gas is circulated as a counter current to the lime.

By this means bleaching powder is obtained containing about 35 per cent. of its weight of active chlorine.

It is, however, slowly decomposed by CO_2 in air with the liberation of Cl, and is decomposed more readily under the effect of heat and sunlight, so that the powder should never be stored in hermetically sealed vessels.

This liberation of chlorine by exposure to air makes bleaching powder useful as a disinfectant, and it is sold for this purpose under the name of "chloride of lime."

The constitution of bleaching powder has been the subject of many researches and discussions, but it is now usually considered to be a mixture of calcium chlorohypochlorite, $CaOCl_2$, mixed with free lime, $Ca(OH)_2$. It is decomposed by the action of water, which gives an alkaline solution owing to the presence of free calcium hydroxide, forming calcium chloride and calcium hypochlorite in solution, and is also decomposed by acids, and carbon dioxide thus:

$$2CaOCl_2 \rightarrow CaCl_2 + Ca(OCl)_2$$
$$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$$
$$CaOCl_2 + CO_2 \rightarrow CaCO_3 + Cl_2$$

Use of bleaching powder in the bleaching of cotton. Bleaching powder is principally employed for the bleaching of cotton goods, the material being first boiled with a solution of sodium hydroxide (or lime and hard resin soaps may be used) to remove impurities, such as natural cotton wax and grease or other substances which become associated with the fibre during the manufacture. This treatment brings the fibre into a state in which it is easily attacked by the chlorine, and is known as **bowking.** It is usually carried out in large iron boilers known as kiers. The cotton is then passed into a clear dilute solution of bleaching powder (1° Tw.), made by grinding bleaching powder with water, and filtering through cotton cloth, or settling in tanks. After standing in this solution for two or three hours, the cotton is taken out and the solution removed from the fibre by squeezing, the whole process being known as **chemicking.**

The material is next passed into very dilute sulphuric acid (1·5° Tw.), the process being known as **souring.** This decomposes any bleaching powder which may remain in the fibre, and at the same time completes the bleaching action by the liberation of chlorine. The excess of acid is finally completely removed by a thorough washing in running water. In this way the cotton is made quite white, although at the start it may have had a grey appearance.

Chlorine has quite a different action on wool, and instead of the material being bleached it becomes yellow in colour. The chlorine has also some action on the wool fibre itself, and the characteristic scaly character (see Chapter XXXIII), which is readily seen when the fibre is examined under the microscope, is almost destroyed. The scaly character plays an important part in the felting and milling of wool fibres, and the removal of the scales greatly modifies the felting and milling properties. Since the shrinking of woollen fabrics on washing is due to the felting properties of the fibres, the removal of these properties tends to render the fabrics unshrinkable (p. 316). The following experiment will illustrate this action.

A woollen fent is cut into two pieces and one of these is soaked in a solution of bleaching powder for about half an hour, squeezed off, and placed in dilute hydrochloric acid for 15 minutes. Finally the acid is removed by washing several times in water. The two pieces are then given the same milling treatment by rubbing them alternately between the hands in a strong soap solution to which a small quantity of washing soda has been added. It will be found that the untreated piece becomes quite matted on the surface and shrinks considerably, whilst the untreated portion does not show any signs of matting and does not shrink. The action of chlorine on wool also increases its affinity for many dyestuffs.

Oxides and oxy-acids of chlorine.

Chlorine forms two oxides: **chlorine monoxide, Cl_2O,** which is prepared by the action of chlorine on dry mercuric oxide in the cold,

$$2HgO + 2Cl_2 \rightarrow HgO, HgCl_2 + Cl_2O$$

and **chlorine peroxide, ClO_2,** which is prepared by gradually adding potassium chlorate to strong sulphuric acid heated gently on a water bath.

$$3KClO_3 + 2H_2SO_4 \rightarrow KClO_4 + 2KHSO_4 + H_2O + 2ClO_2$$

Chlorine monoxide is a yellow gas, extremely unstable and decomposes with explosive violence on heating slightly. It can be condensed to an orange coloured liquid at − 20° C.

The peroxide is a yellow, heavy gas with an unpleasant odour. It is very unstable and is extremely explosive, and should never be prepared *except in very small quantities.* It is a very powerful oxidising agent, phosphorus and carbon taking fire spontaneously when brought into contact with the peroxide.

The chief oxy-acids of chlorine are hypochlorous acid, $HClO$, chloric acid, $HClO_3$, and perchloric acid, $HClO_4$.

Hypochlorous acid, $HClO$, is formed from the monoxide by solution in water, and can be obtained by preparing the monoxide in presence of water, *e.g.*, by passing a stream of chlorine gas through water in which mercuric oxide is suspended.

It is an unstable acid and can only be obtained in dilute solution, but its salts with the alkalis are more stable. They are prepared by passing a stream of chlorine through solutions of the alkalis in the cold.

$$Cl_2 + 2NaOH \rightarrow NaCl + NaClO + H_2O$$

Hypochlorous acid is a good oxidising agent and has a powerful bleaching action.

Electrolytic bleaching liquor. Sodium hypochlorite is now made by the electrolysis of brine and is known as "electrolytic bleach liquor." The cells for this process are usually made of stone or earthenware and the electrodes of an alloy of platinum and iridium, or of carbon. The sodium chloride is decomposed into its elements, the sodium forming caustic soda with the water, and this reacts with the chlorine to form sodium hypochlorite as shown above. The solution must be kept cool to prevent decomposition. Only weak solutions containing 1—3 per cent. of available chlorine can be prepared, and, since from 4 to 10 tons of sodium chloride (depending on the apparatus used) are required for the production of 1 ton of chlorine, the process is comparatively expensive. It is stated, however, that $\frac{3}{4}$ lb. of electrolytic chlorine will do the work of 1 lb. of bleaching powder chlorine, and under some conditions electrolytic chlorine is stated to be cheaper than the use of bleaching powder.

Chloric acid, $HClO_3$, is made by the action of sulphuric acid on a solution of barium chlorate:

$$Ba(ClO_3)_2 + H_2SO_4 \rightarrow 2HClO_3 + BaSO_4$$

The insoluble barium sulphate is filtered off and the solution of chloric acid concentrated in vacuo.

It is an unstable acid and a strong oxidising agent. Its salts are much more stable and can be obtained by passing a stream of chlorine through hot solutions of the alkalis, potassium chlorate being obtained thus:

$$6KOH + 3Cl_2 \rightarrow 5KCl + KClO_3 + 3H_2O$$

Perchloric acid, $HClO_4$, is obtained on the distillation of a mixture of potassium perchlorate and strong sulphuric acid. Like the other oxy-acids of chlorine it is unstable, but its salts are more stable. Potassium perchlorate is prepared by gently heating potassium chlorate until the fused mass becomes pasty and then separating from the potassium chloride by crystallisation, the chloride being much more soluble than the perchlorate.

$$2KClO_3 \rightarrow KCl + KClO_4 + O_2$$

CHAPTER XIX

SULPHUR AND ITS COMPOUNDS

SULPHUR: SULPHURETTED HYDROGEN AND SULPHIDES: OXIDES AND OXY-ACIDS OF SULPHUR: SULPHURIC ACID: CONTACT AND CHAMBER PROCESSES OF MANUFACTURE: SULPHATES, SULPHITES, BISULPHATES AND BISULPHITES: CARBONISING: PERSULPHURIC ACID AND PERSULPHATES: SODIUM THIOSULPHATE: HYDROSULPHITES AND FORMALDEHYDE HYDROSULPHITES USED IN TEXTILE INDUSTRIES.

Sulphur: Symbol, S; atomic weight, 32.

Occurrence. Sulphur occurs in nature both in the free state and combined with metals. In the combined state, it occurs chiefly as sulphides and sulphates, *e.g.*, galena or lead sulphide, PbS, zinc blende or zinc sulphide, ZnS, iron pyrites or iron sulphide, FeS_2, barytes or barium sulphate, $BaSO_4$, and gypsum or calcium sulphate, $CaSO_4, 2H_2O$.

In the free state the sulphur is generally associated with volcanic or igneous rocks, occurring as a coating on the rock or filling crevices and cracks.

It is extracted from this latter form of native sulphur by melting the sulphur, and allowing it to run from the earthy matter. The crude sulphur obtained in this way is not pure, and is distilled in an iron retort, the vapour being condensed in a large brick chamber. If the distillation is carried on slowly so that the condensing chamber remains cool, or if the chamber is cooled by artificial means, the sulphur condenses in the form of a fine powder, usually known as "flowers of sulphur." When the distillation is allowed to proceed more rapidly, so that the walls of the condensing chamber become hot, the sulphur collects in the form of a liquid on the bottom of the chamber, which has a sloping floor. When a quantity of sulphur has collected, it is tapped off in a suitable manner, and run into cylindrical moulds, the sulphur so obtained being known as "roll sulphur."

Allotropic forms of sulphur. Sulphur occurs in the following chief allotropic varieties, though other forms have recently been described:

(1) **α Sulphur or rhombic sulphur.** This is obtained by dissolving roll sulphur in carbon disulphide, and then allowing the solution to eva-

porate slowly in a deep beaker. Large clear yellow crystals of *a* sulphur are obtained.

(2) **β Sulphur or monoclinic sulphur.** *β* sulphur is obtained by melting a small quantity of roll sulphur carefully in a large clay crucible, about 4 in. high, and allowing it to stand in the air until a crust forms on the surface. Two holes are then bored in the crust by a hot rod, and the sulphur which has not crystallised is poured off. If the crust is then removed the monoclinic sulphur will be seen adhering to the sides of the crucible, and to the under part of the crust, in long, clear, yellow needle-shaped prisms. On standing for some time these clear crystals become quite opaque, and the properties of the sulphur become those of the *a* variety.

(3) **γ Sulphur or plastic sulphur.** This is prepared by quickly cooling molten sulphur, heated to about 350° C. When the roll sulphur is first melted, at about 115° C., it forms a very mobile amber-coloured liquid, rapidly darkening in colour on heating until at 200° C. it is almost black, and so viscid that the sulphur will scarcely flow. At about 300° C. it will flow slowly and is lighter in colour. If then poured into water in a fine stream, the plastic sulphur is obtained in long yellow elastic strings and is quite transparent. It slowly changes into the *a* variety, the strings losing their elasticity, and become quite brittle and opaque.

(4) **δ Sulphur or milk of sulphur.** *δ* sulphur is obtained as a white powder when hydrochloric acid acts on a solution containing calcium polysulphides, or when sulphur is precipitated by passing sulphuretted hydrogen into an oxidising agent.

The properties of the allotropic modifications of sulphur are shown in the following table:

	a sulphur	*β* sulphur	*γ* sulphur	*δ* sulphur
Shape	rhombic crystals	monoclinic prisms	elastic, amorphous	amorphous, whitish
Melting point	114·5° C.	119° C.	—	—
Specific gravity	2·05	1·96	1·95	—
On standing	permanent	changes to *a*	changes to *a*	permanent
Solubility in carbon disulphide	soluble	insoluble	insoluble	soluble

Sulphur is used in the manufacture of matches, gunpowder, dyestuffs, for the production of sulphur dioxide for bleaching wool and for the manufacture of sulphuric acid. All the forms of sulphur burn in oxygen or air, with the production of sulphur dioxide. Milk of sulphur is used in pharmacy.

Sulphuretted hydrogen, hydrogen sulphide or hydrosulphuric acid, H_2S.

Preparation. Sulphuretted hydrogen is formed in small quantities when a stream of hydrogen is passed through boiling sulphur. Pure sulphuretted hydrogen is made by gently heating strong hydrochloric acid with antimony sulphide.

$$Sb_2S_3 + 6HCl \rightarrow 2SbCl_3 + 3H_2S$$

It is nearly always prepared, however, by the action of dilute sulphuric or hydrochloric acid on ferrous sulphide, an apparatus similar to that used for the preparation of hydrogen being employed.

$$FeS + 2HCl \rightarrow FeCl_2 + H_2S$$

Sulphuretted hydrogen prepared in this way is always impure, containing hydrogen, and traces of other gases, due to the presence of iron in small quantities in commercial ferrous sulphide.

Properties. Sulphuretted hydrogen is a colourless gas, with a sweetish taste and a very offensive odour. It can be liquefied at −62° C. It is soluble in water, one volume of water at 15° C. dissolving three volumes of the gas. The solution, which is acid in character, is used as a reagent in the laboratory, but on standing is slowly oxidised with the precipitation of sulphur. If breathed in large quantities it is poisonous. It burns in a free supply of air with a blue flame, with the formation of water and sulphur dioxide:

$$2H_2S + 3O_2 \rightarrow 2H_2O + 2SO_2$$

If the supply of oxygen is limited, the sulphur is deposited in the solid condition, or may be partially converted into SO_2:

$$2H_2S + O_2 \rightarrow 2H_2O + S_2$$

The gas also reacts with sulphur dioxide and chlorine, depositing sulphur, thus:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$
$$H_2S + Cl_2 \rightarrow 2HCl + S$$

Uses. Sulphuretted hydrogen is used principally as a laboratory reagent, and also for the preparation and manufacture of sulphides.

Sulphides. Sulphuretted hydrogen is a weak acid and forms salts, known as sulphides. Many metallic sulphides occur in nature in the form of minerals, *e.g.*, galena, PbS; zinc blende, ZnS; iron pyrites, FeS_2, etc.

Sodium sulphide. One of the most important of these sulphides is sodium sulphide. This is made on a large scale by reducing sodium sulphate by carbon (usually coal) at a high temperature. The sodium sulphide is extracted with water and the solution concentrated. If the concentrated solution is allowed to cool, crystals of $Na_2S, 10H_2O$ separate, but if the concentration is carried on until the solution contains 50—60 per cent. of sodium sulphide, the solution sets to a solid mass on cooling. In this latter form it is known as **"rock" sodium sulphide.** It is rarely made stronger than 65 per cent. commercially, as above that strength it is liable to take fire spontaneously owing to oxidation.

Sodium sulphide is used extensively as a depilatory in tanning (removal of hair from skin), for the manufacture of sulphide dyestuffs and as a solvent for these dyestuffs during the process of dyeing.

Ammonium sulphide. This is prepared by dividing a quantity of dilute ammonium hydroxide into two equal portions, and saturating one part with sulphuretted hydrogen, thus forming ammonium sulphydroxide:

$$NH_4OH + H_2S \rightarrow NH_4SH + H_2O$$

This is then mixed with the untreated portion of NH_4OH, thus forming the colourless ammonium sulphide, $(NH_4)_2S$:

$$NH_4SH + NH_4OH \rightarrow (NH_4)_2S + H_2O$$

The colourless solution gradually turns yellow, through decomposition and liberation of sulphur, which dissolves in the ammonium sulphide, forming polysulphides, $(NH_4)_2S_2$, $(NH_4)_2S_3$, etc.

The so-called **yellow ammonium sulphide** is prepared by dissolving the proper quantity of flowers of sulphur in the colourless $(NH_4)_2S$, according to the equation:

$$(NH_4)_2S + S \rightarrow (NH_4)_2S_2$$

Other metallic sulphides. Many of the sulphides have characteristic colours, *e.g.*, MnS, pink; As_2S_3, bright yellow; CdS, lemon yellow; Sb_2S_3, orange red; SnS_2, dirty yellow; SnS, dark brown; and as these sulphides are insoluble in water, the precipitation of these, as characteristically coloured sulphides, when H_2S is passed into solutions containing the metals, is used in analytical work for the detection and separation of these metals.

Oxides and oxy-acids of sulphur.

Oxides	**Oxy-acids**
Sulphur dioxide, SO_2	Sulphurous acid, H_2SO_3
Sulphur trioxide, SO_3	Sulphuric acid, H_2SO_4
	Pyrosulphuric acid Nordhausen sulphuric acid, Fuming sulphuric acid or oleum $H_2S_2O_7$ or $H_2SO_4+SO_3$
	Thiosulphuric acid, $H_2S_2O_3$
Sulphur sesquioxide, S_2O_3	Hyposulphurous acid or hydrosulphurous acid $H_2S_2O_4$
Sulphur heptoxide, S_2O_7	Persulphuric acid, $H_2S_2O_8$

In addition to the above, there are other oxy-acids, known as thionic acids, which are of less importance.

Sulphur dioxide. Preparation. Sulphur dioxide is formed when sulphur or certain sulphides are burnt in air or oxygen.

It can be prepared by the action of hot concentrated sulphuric acid on copper, lead, mercury and certain other metals, also on sulphur and carbon; it can also be obtained by the action of dilute acids on sulphites, thiosulphates and bisulphites, the following equations representing the actions:

$$Cu + 2H_2SO_4 \rightarrow SO_2 + CuSO_4 + 2H_2O$$

The reaction is probably more complex than is shown by this equation, as some cuprous sulphide is also formed.

$$S + 2H_2SO_4 \rightarrow 3SO_2 + 2H_2O$$

$$C + 2H_2SO_4 \rightarrow 2SO_2 + CO_2 + 2H_2O$$

$$\underset{\text{sodium sulphite}}{Na_2SO_3} + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2$$

$$\underset{\text{sodium bisulphite}}{NaHSO_3} + H_2SO_4 \rightarrow NaHSO_4 + H_2O + SO_2$$

$$\underset{\text{sodium thiosulphate}}{Na_2S_2O_3} + H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + S + H_2O$$

The figure (Fig. 69) shows the method of preparing SO_2 and converting into liquid SO_2 by a freezing mixture. Sulphur dioxide may be readily prepared for laboratory purposes by allowing concentrated sulphuric acid to drop on to a saturated solution of sodium bisulphite. The bisulphite is placed in a generating flask and the acid allowed to drop from a tap funnel. In this manner a continuous current of sulphur dioxide can be obtained.

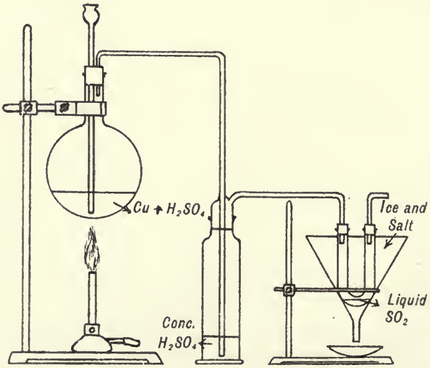


Fig. 69. Preparation of liquid SO_2.

On the large scale sulphur dioxide is made by burning iron pyrites in specially constructed kilns.

Properties. Sulphur dioxide is a colourless gas, is heavier than air, and has a suffocating odour. It can be condensed to a liquid by cooling to − 10° C. with a freezing mixture of ice and salt, or by submitting the gas at the ordinary temperature to a pressure of about three atmospheres. Sulphur dioxide is very soluble in water, one volume of water at 0° C. dissolving 80 volumes of the gas. At higher temperatures it is less soluble, one volume of water at 15° C. dissolving only 40 volumes of sulphur dioxide, the solution containing sulphurous acid. Sulphur dioxide is a powerful reducing agent and will reduce chromates and dichromates to chromium salts, the yellow and red solutions being turned green.

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

A solution of potassium dichromate on filter paper serves as a test for the presence of sulphur dioxide in a gas, but since other gases will give this reaction the test is not conclusive.

Sulphur dioxide will also reduce purple-coloured potassium permanganate to practically colourless salts of potassium and manganese.

$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

Sulphur dioxide is oxidised by hydrogen peroxide to sulphur trioxide and this in the presence of water forms sulphuric acid.

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$

Sulphur dioxide as an anti-chlor. In the presence of water sulphur dioxide reacts with chlorine to form hydrochloric and sulphuric acids.

$$SO_2 + Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$$

It is therefore used for removing the last traces of chlorine from fibres which have been bleached with chlorine, and in this capacity is known as an "anti-chlor." The removal of chlorine is in many cases necessary owing to the destructive action of chlorine on prolonged treatment.

Sulphur dioxide as a bleaching agent. Sulphur dioxide is a mild bleaching agent, and is used for decolorising fibres which are affected by the action of chlorine, *e.g.*, wool, silk and straw.

The **bleaching of wool** with sulphur dioxide is known as **stoving**, and is carried out in the following manner. The wool is first cleaned by scouring, and after washing well with clean water is exposed in the moist condition to the fumes of burning sulphur. This is done in closed chambers, in which sulphur is burnt in iron pots or brick pans. The amount of sulphur must be regulated according to the size of the chamber, as, if the flame dies out and an excess of sulphur remains in the pot, the sulphur may be sublimed and yellow stains may be produced on the wool. 1 lb. S requires 56¼ cu. ft. of air for complete combustion. The wool is left in contact with the gas for several hours, and is then washed well. Since any sulphur dioxide remaining in the fibres may cause defects in dyeing, it is advantageous to after-treat the wool with a dilute solution of hydrogen peroxide to oxidise the sulphur dioxide to sulphuric acid, which is removed by washing.

Sulphur trioxide is always formed to a small extent in the burning of sulphur in air, and with water this will form sulphuric acid. If the chamber contains iron fittings, the iron will be corroded by the acid formed. The acid also retards the bleaching action to some extent. The wool becomes somewhat harsh by the above treatment, but washing with soap and water remedies this.

The effect of sulphur dioxide on wool may be shown by the following experiment. Take some wool from the stove and divide into two portions. One portion is washed with water, and then dyed with ·1 per cent. (calculated on the weight of wool) of magenta dissolved in H_2O (amount of $H_2O = 30$ times weight of wool). The other portion is treated with water and then placed in a bath, containing 5 c.c. of hydrogen peroxide in 100 c.c. H_2O, made just alkaline to litmus with ammonia, for 15 minutes. It is then washed with water and dyed with ·1 per cent. magenta in a similar manner to the first sample. If, after several days, the dyed patterns are compared, it will be found that the untreated pattern has faded to some extent. The action of sulphur dioxide as a bleaching agent on wool is not very permanent, and on exposure to air and light the wool gradually regains its colour. Sulphur dioxide only acts as a bleaching agent in presence of moisture. Probably the bleaching is due to the nascent hydrogen liberated by the action of the sulphur dioxide on water, the hydrogen reducing the colouring matter to a colourless compound.

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + \underset{\text{nascent}}{2H}$$

Sulphurous acid, sulphites and bisulphites. Sulphurous acid is formed as an unstable acid in solution, whenever SO_2 is dissolved in water, though the solution may also contain uncombined sulphur dioxide.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

The acid is unstable and readily evolves SO_2, even at ordinary temperatures, and rapidly on boiling. It has bleaching properties similar to gaseous sulphur dioxide.

It forms salts known as sulphites and bisulphites, but only the alkali compounds are of importance commercially.

Sodium bisulphite. This is obtained by saturating a solution of caustic soda or sodium carbonate with sulphur dioxide.

$$NaOH + SO_2 \rightarrow NaHSO_3$$
$$Na_2CO_3 + H_2O + 2SO_2 \rightarrow 2NaHSO_3 + CO_2$$

It is commonly sold in solution, containing about 40 per cent. $NaHSO_3$, and is used as a bleaching agent, the goods being treated with a solution of bisulphite and dilute hydrochloric acid, either separately or mixed together, so that it is the liberated sulphurous acid which brings about the bleaching action.

$$NaHSO_3 + HCl \rightarrow H_2SO_3 + NaCl$$

Sodium sulphite. Sodium sulphite may be prepared by neutralising sulphurous acid with caustic soda in the proportions shown in the equation.

$$2NaOH + H_2SO_3 \rightarrow Na_2SO_3 + 2H_2O$$

It may also be prepared by boiling off SO_2 from a solution of the acid sulphite, and then crystallising the salt from the solution.

$$2NaHSO_3 \rightarrow Na_2SO_3 + SO_2 + H_2O$$

Sulphur trioxide. Preparation. Sulphur trioxide may be prepared by distilling fuming sulphuric acid and condensing the vapour in a well-cooled flask.

By treating sulphuric acid with phosphorus pentoxide, water is removed from the sulphuric acid and sulphur trioxide is liberated.

Sulphur trioxide is best prepared by passing a mixture of approximately two volumes of sulphur dioxide and one volume of oxygen over platinised asbestos heated to about 400° C., as shown in Fig. 70. This reaction forms the basis of the manufacture of sulphuric acid by the "contact process."

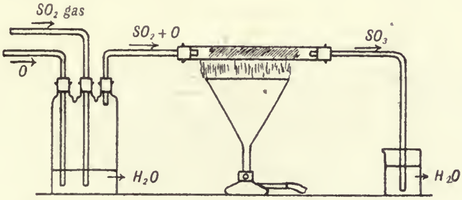


Fig. 70. Preparation of sulphur trioxide and conversion into sulphuric acid.

Properties. Sulphur trioxide crystallises in long silky prisms, and exists in two forms, αSO_3, melting at 15° C., and βSO_3, melting at 25° C. The latter is probably S_2O_6. Both forms have a great affinity for water, dissolving with the formation of sulphuric acid.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Sulphuric acid.

There are two processes in use for the manufacture of sulphuric acid, the **contact process**, used largely in Germany and America, and the **chamber process**, used principally in Britain.

The contact process. This process is based on the above method for preparing sulphur trioxide by passing a mixture of sulphur dioxide and oxygen over heated platinised asbestos. The sulphur dioxide is made by burning iron pyrites, and is then carefully purified from all traces of arsenic, finely-divided sulphur, dust, and mist of sulphuric acid. These substances, particularly arsenic, act as "contact poisons," and soon paralyse the action of the platinum. This purification is accomplished by scrubbing the gases with steam and water and finally drying them.

The sulphur dioxide must also be mixed with an excess of air in order to obtain a good yield of SO_3.

The mixed gases are passed around the contact tubes before being passed over the contact material (Fig. 71), and in this way the heat produced in the chemical action between the SO_2 and O is made use of in giving the gases a preliminary heating. By this means the temperature of the contact material is kept steady at about 400° C.—450° C., an essential condition in producing a yield of 98 per cent.

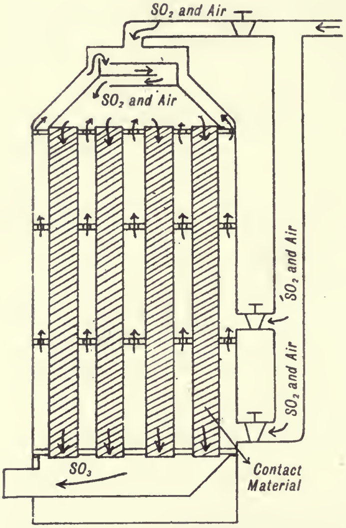


Fig. 71. Contact oven for manufacture of sulphuric acid.

Other contact materials are in use, such as pyrites cinder (Fe_2O_3), chromic oxide, nickel sulphate, etc., but are not so efficient as platinum, and in some cases the oxidation of the SO_2 is started by ferric oxide and finished by platinum.

The white mist of sulphur trioxide is dissolved completely in water with some difficulty, although it has such a powerful affinity for water, but is very readily absorbed in 97—98 per cent. sulphuric acid. In producing ordinary concentrated sulphuric acid, water is added as required in order to maintain the strength of the acid at 98 per cent.

Fuming sulphuric acid or "oleum" (Nordhausen sulphuric acid or pyrosulphuric acid), H_2SO_4, SO_3 or $H_2S_2O_7$. Concentrated sulphuric acid will combine with another molecule of sulphur trioxide forming the pyrosulphuric acid, $H_2S_2O_7$, or H_2SO_4, SO_3, a white crystalline solid, containing 90 per cent. total SO_3 and 45 per cent. of "free SO_3." This acid was at one time manufactured at Nordhausen by the distillation of ferrous sulphate crystals.

The acid is now put on the market in various strengths under the terms fuming sulphuric acid or "oleum," usually containing from 87 to 92 per cent. total SO_3, these acids being largely used in the manufacture of artificial dyestuffs.

The acid containing 87 per cent. total SO_3 will contain 13 per cent. water, the latter being in combination with 57 per cent. SO_3 as H_2SO_4, leaving 30 per cent. "free SO_3." Similarly the 92 per cent. acid contains 8 per cent. $H_2O = 36$ per cent. combined SO_3 and 56 per cent. "free SO_3." A table showing the densities of oleums of different strengths will be found in the Appendix (Table 9).

Preparation of sulphuric acid. Sulphuric acid may be prepared on a small scale as shown in Figs. 72 and 73, a method which illustrates the processes taking place in the chamber process for manufacturing sulphuric acid.

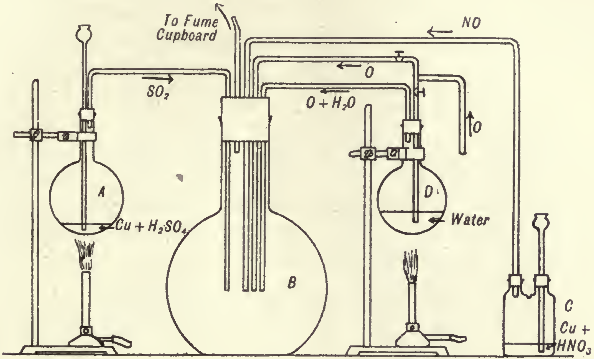


Fig. 72. Preparation of sulphuric acid.

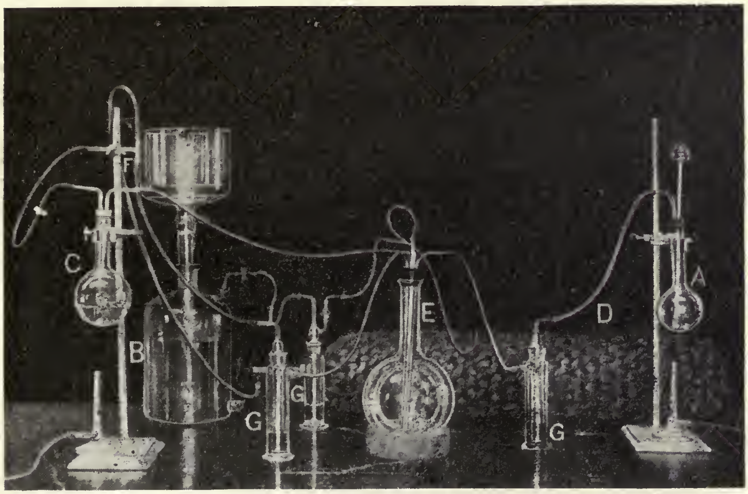


Fig. 73. Preparation of sulphuric acid, illustrating the "chamber" process.
A, flask containing Cu and H_2SO_4; *B*, gasholder containing NO; *C*, flask containing water; *D*, oxygen cylinder; *E*, chamber flask; *F*, T-tube; *G*, wash bottles.

Sulphur dioxide is prepared from copper and sulphuric acid in the flask, *A*, Fig. 72, or a syphon of liquid SO_2 may be used as the source of the gas, the SO_2 being preferably passed through a wash bottle containing concentrated H_2SO_4 to time the speed of the gas, and then delivered into the large flask, *B*, representing the "chamber." Nitric oxide is passed from a separate generator, *C*, containing copper and dilute nitric acid, into the chamber, *B*. Oxygen from a gas cylinder is passed through a T-tube directly into the flask, *B*, and also through water in the flask, *D*, into the chamber, *B*.

The following reactions take place in the flask, *B*:

$$NO + O \rightarrow NO_2$$
$$NO_2 + SO_2 + H_2O \rightarrow H_2SO_4 + NO$$

With a deficiency of steam a crystalline solid may be formed known as nitro-sulphuric acid, or nitrosyl sulphate, $H(NO)SO_4$, or $SO_2(OH)(NO_2)$. This is commonly known as **chamber crystals**, and its formation is evidence of deficiency of steam in the commercial process, the compound being probably formed and decomposed thus:

$$2SO_2 + 2NO_2 + H_2O + O \rightarrow 2SO_2(NO_2)(OH)$$
$$2SO_2(OH)(NO_2) + H_2O \rightarrow 2SO_2(OH)_2 + N_2O_3$$

The formation of the crystals may be shown in the following manner. The air in the chamber flask, *B*, is expelled by oxygen passed directly into the flask, and the supply of oxygen is then stopped. SO_2 and NO are passed into the flask until the gas is dark brownish-red, the gases are then stopped, and a small quantity of water vapour is passed in by allowing the oxygen to pass through hot water in the flask, *D*. The sides of the flask, *B*, will become covered with a white crystalline solid. The remaining gas is then expelled by oxygen, and more steam is passed in by boiling the water in the flask, *D*. The crystals will decompose with effervescence, the gas becoming dark red through the liberation of the oxides of nitrogen.

In the commercial process, the actions taking place are very complex, and the above reactions must only be considered to be typical of the actual ones.

Manufacture by the chamber process. By far the greater portion of the ordinary concentrated sulphuric acid is made in Britain by this process, shown diagrammatically in Fig. 74, which depends essentially on the oxidation of sulphur dioxide by the oxygen of the air, nitrogen peroxide acting as the carrier of oxygen. The sulphur dioxide is produced by burning roll sulphur, iron pyrites, or spent oxide of iron (containing about 60 per cent. free sulphur) obtained from gas works, in air in pyrites burners. In modern burners, the pyrites is made to travel gradually through the furnace as a counter-current to the air entering the furnace.

As the sulphur dioxide passes into the chamber it is mixed with nitric acid vapour, the nitric acid being prepared by the action of sulphuric acid on sodium nitrate in nitre pots arranged in the flue, or the acid is separately prepared in a suitable still. The nitric acid and sulphur dioxide react to form nitrogen peroxide and sulphuric acid, thus:

$$SO_2 + 2HNO_3 \rightarrow H_2SO_4 + 2NO_2$$

The gas from the pyrites burners is usually supplied to the chambers by two channels, one portion being mixed with the nitric acid, and the other passing through the "Glover tower" referred to later. The gases in the leaden chambers are supplied with steam or a spray of water, and the main formation of sulphuric acid takes place, according to the equations given under the preparation above.

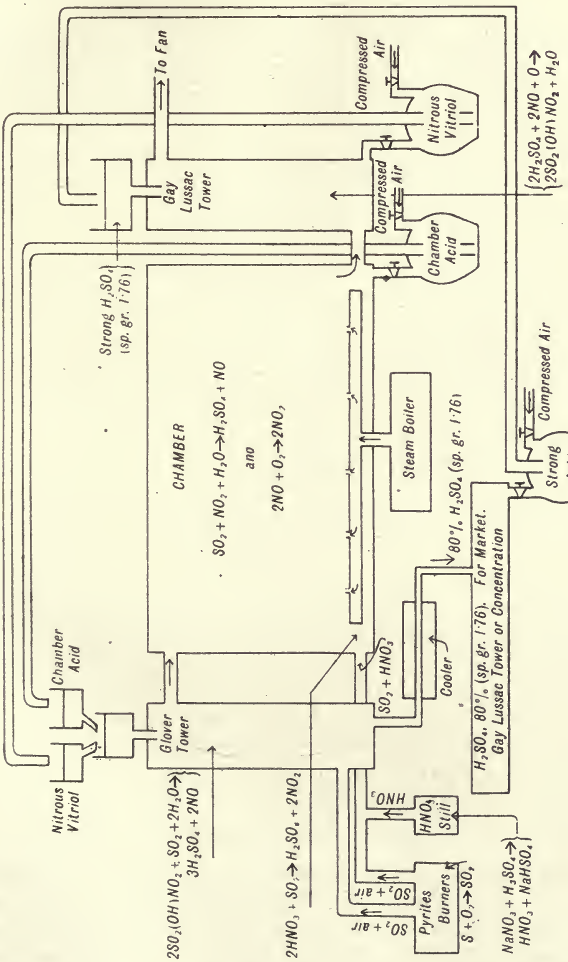


Fig. 74. Diagrammatic view of manufacture of sulphuric acid.

Several chambers are employed and are connected in series, the number varying in different works, and the sulphuric acid collects at the bottom of the chambers as dilute sulphuric acid, known as **chamber acid** (sp. gr. 1·5—1·6).

Finally practically the whole of the sulphur is converted into sulphuric acid, and nitrous fumes and nitrogen pass away from the last chamber. The nitrous fumes are largely recovered by passing the gases through the **Gay Lussac tower**, through which strong acid is falling over acid-resisting material. The acid absorbs the oxides of nitrogen with the formation of **nitrous vitriol**, which contains nitro-sulphuric acid, thus:

$$2H_2SO_4 + 2NO + O \rightarrow 2SO_2(OH)(NO_2) + H_2O$$

The chamber acid and nitrous vitriol are separately collected in tanks, and from time to time are run into containers (**eggs**) and blown by compressed air to the top of the **Glover tower**. In modern forms of apparatus, the acid is being blown at regular intervals, the acid running into the egg, and, by means of a float, the compressed air is admitted when the acid reaches a certain level in the egg, the supply of acid being simultaneously cut off.

The chamber acid and nitrous vitriol are suitably sprayed or distributed in the top of the "Glover tower" on to acid-resisting material, and the falling acid meets the hot ascending gases direct from the pyrites burners.

The tower thus serves (*a*) to cool the gases, (*b*) to concentrate the chamber acid, (*c*) to denitrify the nitrous vitriol, the nitrous gases passing back into the chamber. The strong acid (sp. gr. 1·73, 80 per cent. H_2SO_4) delivered from the bottom of the "Glover tower" is passed through lead pipes or channels, cooled by a counter-current of water, and stored in the strong acid tank as **brown oil of vitriol** (B.O.V.).

A great portion of this acid finds its way into commerce as B.O.V., and if stronger or pure acid is required it is concentrated and purified as detailed below.

In some of the most modern works, small scrubbing towers are placed between the chambers, this method serving to thoroughly mix the gases, whilst diminishing the number of chambers required for efficient working. A good stream of chamber acid flows continuously from each tower.

In theory, the whole of the nitrogen oxides should be recovered in the "Gay Lussac tower," but in actual practice there is always some loss due to the reduction of the nitrogen oxides to nitrogen or nitrogen monoxide, which are not absorbed and result in loss, so that a small but continuous supply of nitric acid must be maintained.

The whole process is illustrated diagrammatically in Fig. 74.

Concentration of sulphuric acid. Many methods of concentrating sulphuric acid have been adopted at different periods, one of the earliest methods being to heat the acid in large glass retorts. The water and a small percentage of the acid distil over, leaving concentrated acid in the retorts. Later platinum stills were used, but these have now been entirely displaced.

In a more modern method the 80 per cent. acid is delivered into a short rectifying tower, where the acid gradually falls from one plate to another meeting hot ascending gases from a gas producer, in which good quality coke is being burnt. The hot acid leaving the tower is cooled, and runs away as concentrated acid (98 per cent.), known commercially as **double oil of vitriol** (D.O.V.).

In the most modern form of concentrating plant, the cascade principle is employed, and the vessels used are made of silica ware or an acid-resisting metal (ferro-silicon), such as "Narki" metal, etc.

The vessels are arranged in cascade as shown in Fig. 75, so that the acid runs from one vessel to the next below, and the hot gases from a fire come into direct contact with the vessels. The acid is finally cooled in a vessel of similar material.

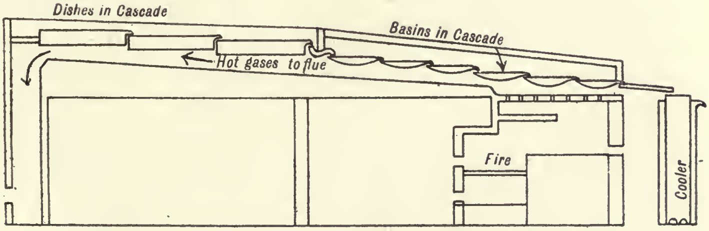


Fig. 75. Concentration of sulphuric acid by cascade process.

Properties. Sulphuric acid is, when pure, a colourless oily liquid, and has a specific gravity of 1·838. The following densities of strong acid show, however, that it is not safe to accept the density of concentrated acid as a criterion of purity, and the strength of the acid should always be obtained by volumetric processes.

Sp. gr. at 15° C.	Strength of acid. Percentage of H_2SO_4 by weight
1·8385	99·95
1·8395	99·45
1·8405	98·70
1·8415	97·70
1·840	95·60
1·839	95·00
1·837	94·20

Ordinary concentrated sulphuric acid contains about 98 per cent. of acid, with 2 per cent. of water. Colourless crystals of pure H_2SO_4 can be obtained by cooling concentrated sulphuric acid by a freezing mixture.

Sulphuric acid boils at 270° C., with slight decomposition, until it attains a strength of about 98 per cent. acid, when it distils with this constant composition, and with a constant boiling point of about 320° C.

Sulphuric acid and water combine together to form several hydrates, and a considerable amount of heat is generated, sufficient to turn a large amount of water into steam.

Care should therefore be taken **never** to pour water into concentrated acid, or it may spurt violently, and in the hot state will cause serious blisters on the skin. To dilute the acid, the acid should always be poured in a slow stream into the water, stirring the mixture well during the pouring, so as to prevent the acid forming a heavy oily layer at the bottom.

This affinity for water is illustrated by the use of concentrated sulphuric acid in desiccators, and in using the strong acid for drying gases. It will also withdraw water from many organic substances and char them, such bodies as paper, sugar, wood, etc., being charred owing to the liberation of carbon.

When mixed with water there is always a contraction in bulk, the maximum contraction of 8 per cent. taking place when about 2 vols. of concentrated acid and 1 vol. of water are carefully mixed.

In making standard sulphuric acid for volumetric purposes, the strength should be found after dilution by actual titration, instead of depending on a factor, calculated from the mixture of known volumes of water and acid of known strength.

Uses of sulphuric acid. Sulphuric acid is used to a considerable extent commercially, and there is scarcely an industry in the country in which it is not applied either directly or indirectly. Large quantities are employed in the manufacture of hydrochloric, nitric and other acids, in the production of explosives, artificial manures, stearin, oleine, sodium sulphate, in the dyeing of wool and silk, carbonising of wool, calico-printing, manufacture of oils, etc., and prior to 1914 considerably over 1 million tons were manufactured in England, and probably nearly an equal amount in each of the countries, Germany, United States, France, with smaller quantities in other countries, such as Japan.

Carbonising of wool. When cotton or cellulose is steeped in dilute sulphuric acid and dried, the cellulose is tendered by conversion into a body termed hydro-cellulose and this is easily removed by mechanical means. The carbonising of wool depends on this action (p. 297). Raw wool invariably contains fragments of vegetable matter which have become entangled in the fibres, known as burrs, and it is almost impossible to remove these by mechanical means. The removal of the cellulose is of importance, as certain classes of dyestuffs will dye wool readily, but are not easily absorbed by cellulose, thus giving rise to light-coloured spots.

The burrs are now entirely removed by the carbonising process, the wool being steeped in 5 per cent. sulphuric acid (1·03 sp. gr.), and then squeezed to remove the excess of liquid. The wool is dried at about

60° C. for 20 minutes to half an hour. At the end of this time the cotton crumbles to dust, and is easily removed by mechanical means.

The acid remaining in the wool is finally neutralised and removed by washing with a dilute sodium carbonate solution (soda ash), and afterwards with water. The removal of the acid is important, as if left in the fibre, it will ultimately become sufficiently concentrated to corrode the wool, and also to affect subsequent dyeing operations. The removal of the soda by washing is also of the greatest importance, or soda stains may be produced in certain operations.

Nitre cake has been suggested for use in carbonising, but has not been very successful for this purpose.

Sulphates and bisulphates. Sulphuric acid, being a dibasic acid, forms two series of salts, namely, sulphates and bisulphates.

The sulphates are mostly soluble in water, the chief exceptions being barium, strontium and lead ; calcium sulphate is sparingly soluble in water.

The sulphates are prepared by one of the following methods :

(1) By dissolving certain metals in sulphuric acid.

(2) By dissolving the basic oxide, hydroxide or the carbonate of the metal in sulphuric acid.

(3) By heating sulphuric acid with certain other salts and evaporating ; or by precipitating the insoluble sulphates by addition of sulphuric acid to a solution of a soluble salt of the metal.

Sodium sulphate. Sodium sulphate is a by-product in the manufacture of nitric acid from sodium nitrate and sulphuric acid, and is also obtained in very large quantities by the action of sulphuric acid on sodium chloride. It crystallises with 10 molecules of water and in this form is known as **Glauber's salt.**

Glauber's salt is used to a large extent in the dyeing industry, and by its aid the fibre takes up the dye more evenly.

It is also used in medicine, and occurs in some of the English and Continental Spa waters.

Sodium bisulphate. This salt is formed in the action of sulphuric acid on sodium chloride at a gentle heat, and is also obtained in the manufacture of nitric acid. This substance under the name "nitre cake" has already been referred to in the manufacture of nitric acid (see Chapter XVII, p. 161). The pure bisulphate is sometimes sold as **tartar substitute** and used in dyeing.

Potassium sulphate. This salt is very similar in properties to the sodium salt and may be prepared similarly. It occurs naturally in the Stassfurt deposits in Germany, principally in combination with other sulphates, and is obtained commercially from these bodies. The crystallised salt has no water of crystallisation.

Ammonium sulphate. Ammonium sulphate is made by passing ammonia, prepared by distillation of gas liquor and lime, into sulphuric acid. The salt forms a constituent of many artificial manures.

Calcium sulphate. Calcium sulphate occurs in nature as gypsum and selenite ($CaSO_4, 2H_2O$). It is slightly soluble in water and is the principal one of the substances giving rise to permanent hardness in water. It can be prepared by treating lime or chalk with sulphuric acid. It is used in dressing and weighting fabrics.

Plaster of Paris is made by partially dehydrating gypsum, the mineral being heated to about 130° C., when it loses three-fourths of its water of crystallisation.

Barium sulphate. Barium sulphate occurs in nature as barytes or heavy spar. It is very insoluble in water, and, in the gravimetric determination of sulphuric acid, the acid is converted by the addition of barium chloride into this salt which is weighed. This method is also used for its preparation.

Barium sulphate is an important constituent in white paint and is also used as a loading for paper, and in dressing fabrics. For the latter purpose it is sold as a paste, under the name **permanent white** or **blanc fixe**.

Magnesium sulphate. Magnesium sulphate occurs in nature in certain mineral waters such as the waters at Epsom. It crystallises with 7 molecules of water, the crystallised compound being known as "Epsom salts." It is used in the finishing of cotton goods, and for this purpose must be free from the chloride, otherwise at high temperatures hydrochloric acid may be liberated which tenders the fibre, due to the following action taking place :

$$MgCl_2 + H_2O \rightarrow MgO + 2HCl$$

It gives a firmness to the fabric, and is not used for soft finishes unless accompanied by a softening agent (see Chapter XXXVIII).

It can be prepared by dissolving the metal or carbonate in dilute sulphuric acid.

Zinc sulphate. Zinc sulphate, sometimes known as white vitriol, is most commonly prepared by the action of dilute sulphuric acid on zinc. It crystallises with 7 molecules of water. It is used for weighting cotton goods, and as an antiseptic for the prevention of mould. It is also used in dyeing and calico printing and in the manufacture of varnishes and paints.

Copper sulphate (blue vitriol). This salt crystallises as $CuSO_4, 5H_2O$, and is best prepared by dissolving metallic copper in concentrated sulphuric acid, dissolving the residue in water, filtering and crystallising. It has been used as a mordant, for fixing certain substantive dyes, in calico printing, and as an oxidising agent in aniline black dyeing.

Ferrous sulphate, $FeSO_4$, $7H_2O$. Ferrous sulphate is used largely in commerce under the name of **green vitriol** or **copperas.** It is made by dissolving iron in dilute sulphuric acid, filtering and crystallising, when it combines with 7 molecules of water. It is largely used in dyeing and tanning, and in the manufacture of inks. It is used as a mordant in the printing of Prussian blue on calico.

Ferric sulphate. This salt can be prepared by the oxidation of ferrous sulphate with nitric acid, in the presence of sulphuric acid, the following action taking place :

$$6FeSO_4+2HNO_3+3H_2SO_4 \rightarrow 3Fe_2(SO_4)_3+4H_2O+2NO$$

It forms double salts with potassium and ammonium sulphates, which crystallise with 24 molecules of water and are known as **potash iron alum** and **ammonium iron alum** respectively.

The **basic ferric sulphate** is used largely as a mordant in dyeing. It is sold under the name of "nitrate of iron," the name being derived from its mode of preparation, though actually the principal compound present is a basic ferric sulphate, $5Fe_2(SO_4)_3$, $Fe_2(OH)_6$. It is made by the action of nitric and sulphuric acids on ferrous sulphate, the amount of sulphuric acid being half the quantity required to form the normal sulphate, thus :

$$12FeSO_4+3H_2SO_4+4HNO_3 \rightarrow 5Fe_2(SO_4)_3, Fe_2(OH)_6+4NO+2H_2O$$

Aluminium sulphate. Aluminium sulphate is obtained by the action of sulphuric acid on precipitated hydrated aluminium oxide (alumina).

It is used in paper-making, in water-proofing, and as a mordant in the dyeing of "Turkey red," but for this purpose it must not contain more than 0·001 per cent. of iron, and should be free from excess of acid. It crystallises as $Al_2(SO_4)_3$, $18H_2O$, but often contains less water than this in the form in which it is sold. It is often known commercially as **cake alum, patent alum** or **concentrated alum.**

Alums. The term "alum" is used to denote a compound having the general formula R_2SO_4, $M_2(SO_4)_3$, $24H_2O$, where R is a monovalent alkali metal or compound radical, and M is a metal which gives a sesquioxide of the formula M_2O_3, *e.g.*, Fe(ic), Al, Cr, Mn(ic).

A series of these compounds may be obtained of which potash alum or ordinary alum, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$, is the type; some of the compounds although known as alums do not contain aluminium. The following are examples :

Potash alum	$K_2SO_4, Al_2(SO_4)_3, 24H_2O$
Chrome alum	$K_2SO_4, Cr_2(SO_4)_3, 24H_2O$
Ammonium alum	$(NH_4)_2SO_4, Al_2(SO_4)_3, 24H_2O$
Iron alum	$K_2SO_4, Fe_2(SO_4)_3, 24H_2O$
Ammonium iron alum	$(NH_4)_2SO_4, Fe_2(SO_4)_3, 24H_2O$

It should be noted that the commercial iron alum is ammonium iron alum.

All the alums may be prepared by crystallising the two sulphates together, and as they crystallise well, taking the cubical form, they are easily got in a state of high purity.

The alums have been largely used in the textile industries. The alums containing aluminium are used in the manufacture of paper, for fire-proofing and water-proofing materials, and for mordanting materials for dyeing, but in some cases they are gradually being replaced by aluminium sulphate.

Other sulphur acids and salts used in textile industries.

Persulphuric anhydride, S_2O_7, and persulphuric acid, HSO_4. Persulphuric anhydride is obtained by the action of the silent electric discharge on a mixture of sulphur trioxide or dioxide and oxygen as a viscous liquid, solidifying on cooling to a transparent crystalline mass. It is a powerful oxidising agent.

The acid is formed in small quantities during the electrolysis of dilute sulphuric acid but is extremely unstable, and cannot be isolated. The salts of persulphuric acid, however, are more stable and can readily be prepared by the electrolysis of bisulphates.

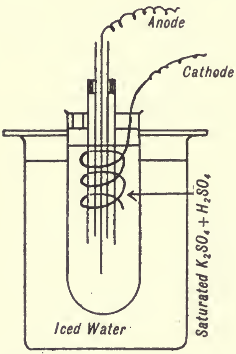


Fig. 76. Preparation of potassium persulphate.

For the production of **potassium persulphate**, the apparatus shown (Fig. 76) is used. A saturated solution of potassium sulphate is dissolved in 30 per cent. sulphuric acid (sp. gr. 1·25), and the liquid is electrolysed as shown with a current of about 2 ampères, using platinum wire electrodes. A white crystalline substance is formed at the anode, and hydrogen is liberated at the cathode.

The persulphates are good oxidising agents, and are used as such in dyeing. The oxygen is liberated from the water, the latter combining with the persulphate when an oxidisable substance is present, thus :

$$2KSO_4 + H_2O \rightarrow 2KHSO_4 + O$$

Thiosulphuric acid and thiosulphates. Thiosulphuric acid is unstable but the sodium salt, **sodium thiosulphate, $Na_2S_2O_3$,** is easily prepared by boiling a solution of sodium sulphite with flowers of sulphur. It is known in commerce as **hyposulphite** or **hypo,** and is used extensively in photography as a fixing agent for removing the unchanged silver salts from negatives and silver prints. Sodium thiosulphate is used as an **anti-chlor** in removing the last traces of chlorine from fibres which have been bleached with this gas.

$$Na_2S_2O_3 + H_2O + Cl_2 \rightarrow Na_2SO_4 + 2HCl + S$$

It is also used in the manufacture of dyestuffs.

With dilute acids sulphur dioxide is liberated and sulphur is deposited.

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + SO_2 + H_2O + S$$

Hydrosulphurous acid and hydrosulphites. The acid is unstable and has not been isolated, but the salts are more stable, and can easily be obtained by the action of zinc dust on sodium bisulphite in the presence of sulphurous acid. **Sodium hydrosulphite** was first given the formula $NaHSO_2$, but Bernthsen has shown it to be $Na_2S_2O_4, 2H_2O$. It is formed by the following reaction:

$$Zn + 2NaHSO_3 + H_2SO_3 \rightarrow Na_2S_2O_4 + ZnSO_3 + 2H_2O$$

Milk of lime is added to precipitate the zinc and neutralise free sulphurous acid, and sodium chloride is afterwards added to the warm concentrated solution to salt out the hydrosulphite, which crystallises as $Na_2S_2O_4, 2H_2O$. This compound is manufactured and sold by the Badische Anilin und Soda Fabric, as **Hydrosulphite, B.A.S.F.**

Messrs Brotherton and Co. Ltd. now supply the above compound as **Sodium hydrosulphite conc. powder.**

The anhydrous compound is obtained by treating the crystalline substance with boiling alcohol, and this is put on the market as **Blankite,** containing 96 per cent. $Na_2S_2O_4$. This compound oxidises in moist air to **sodium metabisulphite,** $Na_2S_2O_5$, and in alkaline solution slowly oxidises to sodium bisulphite, thus:

$$Na_2S_2O_4 + H_2O + O \rightarrow 2NaHSO_3$$

Uses. The compound is a powerful reducing agent, and is used for this purpose in indigo vats for the reduction of indigo to **indigo white.** In this form the dyestuff is readily taken up by the fibre, and on subsequent exposure to air the indigo white is oxidised and the colour fixed on the fibre. The compounds have also found many other uses in the textile industries, in dyeing, bleaching, in the printing of fabrics as a discharging agent, the bleaching of oils, soaps, etc.

For many of these purposes the **hydrosulphites are put on the market in combination with formaldehyde** (see Chapter XXV, p. 262) as very stable compounds, these substances readily decomposing on steaming and liberating the hydrosulphite in the nascent condition, a form in which it is extremely active as a reducing agent. These compounds are dealt with in detail in the chapter on Aldehydes.

CHAPTER XX

CARBON AND SILICON AND THEIR COMPOUNDS

ALLOTROPIC VARIETIES OF CARBON: CARBON DIOXIDE AND CARBONIC ACID: CARBONATES AND BICARBONATES: CARBON MONOXIDE: PRODUCER GAS: WATER GAS: DOWSON GAS: SUCTION GAS: COMBUSTION: ANALYSIS OF FURNACE GAS AND GASEOUS FUELS: SILICON: SILICA AND SILICIC ACIDS: SILICATES: DIALYSIS: "WATER GLASS": KAOLIN: CARBORUNDUM.

Carbon: Symbol, C; atomic weight, 12.

Allotropic forms of carbon. Carbon is one of the most widely diffused of the elements, occurring in the free state but more abundantly in nature in the state of combination. Thus, it is found in all forms of animal and vegetable life, the latter containing approximately 50 per cent. of carbon. The element occurs in three allotropic forms, *viz.*, diamond and graphite, which are crystalline varieties, and various forms of amorphous carbon.

Diamond. The diamond is found in India, Brazil, and South Africa, occurring commonly in a kind of clay known as "blue rock," and the diamonds are extracted by mechanically washing away the earthy matter. Small artificial diamonds have also been prepared by Moissan, amorphous carbon being dissolved in molten iron at the high temperature of the electric furnace, and the iron is then rapidly cooled by immersion in molten lead. The sudden expansion of the iron, caused by cooling and solidification, produces, in the internal portions, enormous pressure. Under these conditions the carbon crystallises, and the diamonds are afterwards extracted by dissolving the iron in dilute acid.

If the diamond is heated to a very high temperature in the electric arc it swells up, and is converted into graphite. Diamond burns in oxygen at a high temperature, forming carbon dioxide and leaving a trace of ash. Diamond is valuable as a gem, its brilliance being due to the high refractive index of the mineral, which brings about reflection of most of the light falling on or entering the crystal. The diamond is the hardest substance known, and it is largely used for grinding and cutting purposes; artificial diamonds are now being used for this purpose. The natural corners of the crystal are the most suitable portions of the mineral for glass-cutting purposes.

Graphite. Graphite, known as plumbago or black lead, which is found at Keswick in England, occurs in bright shining plates easily separated by the point of a penknife.

It burns in oxygen forming carbon dioxide, but leaving a trace of ash, and is therefore a form of carbon. It is used in the manufacture of black lead pencils, for coating metals such as iron to protect them from rusting, for the manufacture of crucibles used in steel making, as a lubricant for machinery and very largely for the manufacture of electrodes. For the latter purpose, **artificial or Acheson graphite** is more commonly employed, which is largely manufactured by heating amorphous carbon, such as coke, with a small percentage of iron oxide in an electric furnace, to a temperature sufficiently high to vaporise the iron and cause crystallisation of the carbon as graphite.

Amorphous carbon. Amorphous carbon occurs in many forms, and in varying degrees of purity. Lamp black, gas carbon, charcoal, coke and coal are all composed essentially of carbon, the amount of impurity as a general rule increasing in the order mentioned.

Lamp black. This is almost pure carbon and is obtained by burning substances which are rich in carbon such as turpentine, $C_{10}H_{16}$, etc., in a supply of air insufficient for complete combustion. Wet coarse blankets are used for condensing the lamp black, or it may be condensed on rotating iron discs cooled by water.

It is mixed with oil for the manufacture of printers' ink, and is also used as a black pigment in paint.

Charcoal. Charcoal is obtained by the dry or destructive distillation of wood, which is heated in retorts out of contact with air.

In the older process of making charcoal, stacks of wood, covered with turf, were partially burnt in a regulated supply of air, the heat converting the remainder of the wood into charcoal. The volatile products of distillation, such as wood spirit, acetone and acetic acid, are lost in this process, but in the more modern method of distilling in iron retorts, these products are collected in the form of a liquid spirit known as **pyroligneous acid**, together with tar. The inflammable gases are also collected and used in the heating of the retorts, whilst the charcoal remains behind in the retorts.

Charcoal is very porous and though its specific gravity is greater than water it floats on the latter owing to the air retained in the pores. Freshly-prepared charcoal possesses the power of absorbing large quantities of gas, the charcoal made from nut shells being particularly good for this purpose. Charcoal made from cocoanut shell will absorb 171 times its volume of ammonia, 86 volumes of nitric oxide, 70 of nitrous oxide, 68 of carbon dioxide and 18 of oxygen. This property of absorbing gases renders charcoal an excellent disinfectant, since the absorbed oxygen reacts with absorbed oxidisable gases in the pores of the charcoal, and thus brings about their decomposition. This property may be strikingly illustrated by the following experiment.

A quantity of powdered charcoal is placed in a bulb tube, with wads of asbestos to retain it in position, and the charcoal is heated for about 15 minutes in a stream of coal gas. The charcoal is then cooled, whilst the coal gas is passing, until the hand may be placed on the bulb, and a stream of sulphuretted hydrogen is then passed through the tube for about 10 minutes, and until the bulb is quite cold. Oxygen is now passed over the charcoal, and the temperature gradually rises until it is sufficiently high to ignite the charcoal, which burns with brilliant sparks in the oxygen gas. This action is due to the absorption of the sulphuretted hydrogen and the oxygen in the pores of the charcoal, in which the molecules are brought into such close contact that they become chemically reactive. The sulphuretted hydrogen is oxidised, and the heat of the reaction is sufficient to raise the temperature of the carbon to its ignition point.

Animal charcoal. Animal or bone charcoal is a very impure form of carbon, and is obtained by the dry distillation of bones. The latter contain a large amount of mineral matter (calcium phosphate, etc.), and this remains behind in the charcoal, the latter usually containing about 10 per cent. of carbon. Animal charcoal possesses in a high degree the power of oxidising certain organic products in solution, and is largely used for decolorising coloured liquids, being used for this purpose in the refining of sugar, and the manufacture of organic compounds ; it is also used in filters for the purification of water.

Coke. Coke is made by the destructive distillation of coal in the manufacture of coal gas, or, for metallurgical processes such as iron smelting in which a hard dense coke is required, it is prepared in specially constructed coke ovens. The coal is heated in retorts or ovens out of contact with air, and the volatile products removed through pipes at the top, the coke being finally removed and quenched with water. Coke varies considerably in appearance and to some extent in composition according to the kind of coal from which it is made, and the temperature at which the decomposition is carried out.

Gas carbon, which is a very pure form of carbon, is obtained as a lining on the roofs and sides of the retorts in gas-making, and is formed by the decomposition of certain dense compounds of carbon and hydrogen. It is a very hard and dense form of carbon and is largely used for the making of electric arc carbons.

Coal. Coal is essentially carbon, combined or associated with varying quantities of hydrogen, oxygen, nitrogen, sulphur, and mineral matter. It has been formed by the slow decomposition of accumulated vegetable matter, locked up in the internal portions of the earth's crust, the decomposition being brought about by the combined influence of pressure and heat.

The following table gives the proportion of carbon in the substances which represent the various stages in the decomposition of vegetable matter.

Substance	Percentage of carbon
Vegetable matter	50
Peat	60
Lignite	70
Coal (average)	80–90
Welsh anthracite	94–95

Oxides of carbon.

There are three oxides of carbon known, which have been prepared in the pure state, *viz.*, carbon dioxide or carbonic anhydride, CO_2, carbon monoxide or carbonic oxide, CO, and carbon suboxide, C_3O_2.

Carbon dioxide. Preparation. Carbon dioxide is always present in the atmosphere to a small extent, being formed during the processes of combustion, respiration, fermentation, putrefaction of organic matter, lime burning, and other chemical processes. It is readily prepared: (1) by the action of heat on any carbonate, with the exception of sodium and potassium carbonates; (2) by burning carbon in an excess of oxygen or air; (3) by heating bicarbonates, such as sodium or potassium bicarbonate; (4) by the action of dilute acids on carbonates.

The latter method is the one most commonly used for its preparation in the laboratory. Calcium carbonate, in the form of marble, is preferably employed, as this gives a steady current of the gas, and dilute hydrochloric acid is added to bring about the reaction (Chapter VI, p. 51).

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

If sulphuric acid is used, the marble becomes coated with an almost insoluble protective crust of calcium sulphate, and the action is soon brought to an end.

Properties. Carbon dioxide is a colourless, heavy gas, with only a faint odour. It does not support combustion and a burning taper is immediately extinguished when placed in the pure gas, or even in air containing about 3 per cent. of CO_2. Magnesium and potassium, however, will burn in the gas with the liberation of carbon.

$$2Mg + CO_2 \rightarrow 2MgO + C$$
$$4K + 3CO_2 \rightarrow 2K_2CO_3 + C$$

It is slightly soluble in water at the ordinary temperature and pressure, but on boiling the solution the carbon dioxide is expelled. The solution exhibits very feeble acid properties and turns blue litmus to a port wine tint. Carbonic acid, H_2CO_3, is present in the solution, but has not been isolated in the pure state, although the salts, carbonates and bicarbonates, are quite stable.

At about four atmospheres pressure at the ordinary temperature of the air, the solubility of carbon dioxide in water is greatly increased, but if the pressure is removed carbon dioxide is rapidly evolved with effervescence. The increased solubility of carbon dioxide under pressure is made use of in the manufacture of soda water and other aerated beverages.

In the presence of sunlight, carbon dioxide is absorbed by chlorophyll, present in the green leaves of plants, trees, etc., and the gas is decomposed, carbon being retained whilst the oxygen is evolved, so that the balance of oxygen and carbon dioxide is maintained in the atmosphere. Carbon dioxide is a very stable gas and is not readily decomposed, though it can be reduced by passing over red-hot carbon to carbon monoxide.

Carbonic acid, carbonates and bicarbonates. Carbonic acid, which is obtained by the combination of carbon dioxide and water, is of very little importance, but its salts are extremely important substances.

With the exception of the alkalis, sodium, potassium, and ammonium, the carbonates are insoluble in water, and all the insoluble carbonates are decomposed on heating into the basic oxide and carbon dioxide.

Sodium carbonate. This salt is known in commerce under a variety of names, the anhydrous form being termed **soda ash** or **pure alkali** and the crystalline form, $Na_2CO_3, 10H_2O$, is commonly known as **washing soda.** It is used on a large scale in all the chemical industries, in dyeing and in the scouring of wool, etc.

It is manufactured by two main processes, the **Leblanc** or **black ash process,** and the **Solvay** or **ammonia-soda process.** In the former process sodium sulphate (salt-cake) is heated with crushed coal and limestone in specially constructed furnaces of the reverberatory type (see Chapter XVIII), or in large cylindrical revolving furnaces, and the mass afterwards extracted with water.

$$Na_2SO_4 + CaCO_3 + 2C \rightarrow Na_2CO_3 + CaS + 2CO_2$$

The salt is afterwards crystallised from the solution as washing soda, and the crystals are drained and purified by recrystallisation if necessary. The crystals are dehydrated, if soda ash is required. In the ammonia-soda process, brine is saturated with ammonia, settled to remove insoluble magnesium compounds as impurities, and the liquid is then passed through a tower divided into chambers by perforated plates. Carbon dioxide is passed upwards through the tower, and passing through the perforations is brought intimately into contact with the liquid. Sodium bicarbonate is precipitated on the plates, and is removed periodically. It is heated to convert it into sodium carbonate, the evolved carbon dioxide being used again in the preparation of further quantities of sodium bicarbonate.

$$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl$$
$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

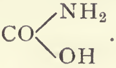
The ammonium chloride formed in the first action may be again used in the preparation of ammonia.

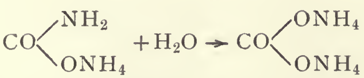
The soda ash or washing soda prepared by the black ash process usually contains caustic soda, sodium sulphide and sodium sulphate as impurities, whereas the "pure alkali" prepared by the ammonia-soda process usually contains traces of salt and sodium bicarbonate only. It contains 58·5 per cent. of Na_2O when pure, and the **pure alkali** is sold under the term **58° alkali**.

A **sesquicarbonate**, Na_2CO_3, $2NaHCO_3$, $2H_2O$, is also put on the market in a very pure state under the name of **crystal soda** or **crystal carbonate**. It separates out on boiling a solution of sodium bicarbonate. Na_2CO_3, H_2O, formed by crystallising from a boiling saturated solution of sodium carbonate is also known as "crystal carbonate," but the product put on the market under this name is mostly the sesquicarbonate.

Potassium carbonate. Potassium carbonate was originally obtained almost exclusively from the ashes of plants by burning the wood in pits or pots and extracting the ashes with water, hence the term "pot-ashes."

Potassium carbonate is also obtained from the **suint** obtained during the washing of wool. The wash water is evaporated and the residue calcined to remove organic matter, the crude potassium carbonate being purified by fractional crystallisation. The potassium carbonate in this case contains less of the sodium salt than that obtained from wood ashes. Potassium carbonate is also obtained by heating potassium sulphate with limestone and carbon in a similar manner to that used for the production of sodium carbonate by the Leblanc process.

Ammonium carbonate. This is obtained by subliming a mixture of ammonium sulphate and chalk and a small amount of charcoal. It is obtained in colourless transparent crystals, which smell strongly of ammonia. The commercial salt is really a mixture of ammonium bicarbonate, NH_4HCO_3, and ammonium carbamate, $NH_4CO_2NH_2$, the ammonium salt of an acid known as carbamic acid,  $CO\genfrac{}{}{0pt}{}{\diagup NH_2}{\diagdown OH}$. The commercial compound is converted into the normal salt by heating with ammonia, thus:



$$CO\genfrac{}{}{0pt}{}{\diagup NH_2}{\diagdown ONH_4} + H_2O \rightarrow CO\genfrac{}{}{0pt}{}{\diagup ONH_4}{\diagdown ONH_4}$$

$$NH_4HCO_3 + NH_3 \rightarrow (NH_4)_2CO_3$$

It is used in dyeing and cleaning, and in medicine.

Magnesium carbonate. This occurs in nature as magnesite, $MgCO_3$, and combined with calcium carbonate in the double carbonate, $CaCO_3$, $MgCO_3$, **dolomite or magnesium limestone**; the carbonates in dolomite are not, however, necessarily present in exact molecular proportions. Pure magnesium carbonate can be obtained by precipitating a solution of magnesium sulphate with sodium carbonate and digesting the product with carbon dioxide. The product obtained on precipitation with sodium carbonate is a basic carbonate, and varies in composition according to the method of preparation. Thus, hot concentrated sodium carbonate gives $Mg(OH)_2$, $4MgCO_3$, $9H_2O$, known as **heavy magnesia,** whereas cold dilute sodium carbonate gives $Mg(OH)_2$, $3MgCO_3$, $3H_2O$, known as **light magnesia.**

Magnesite is largely used in the linings of electric furnaces, and is converted by heat into a sintered mass of magnesia.

Calcium carbonate and bicarbonate. Calcium carbonate, $CaCO_3$, occurs in nature in many forms, such as limestone, marble, chalk, etc.

It can be precipitated in the pure state by the addition of a soluble calcium salt to a soluble carbonate, and is also formed by the combination of carbon dioxide and lime. If carbon dioxide is passed through a clear solution of lime water, a precipitate of calcium carbonate is formed, but if the current of carbon dioxide is continued, the solution gradually becomes clear owing to the formation of soluble calcium bicarbonate, thus:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$$

When the solution of calcium bicarbonate is boiled, carbon dioxide is evolved, and the precipitate of calcium carbonate is re-formed. This is due to the decomposition of the comparatively unstable calcium bicarbonate, thus:

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + CO_2 + H_2O$$

Hardness of water. The temporary hardness of water is due to the presence in the water of calcium or magnesium bicarbonate, as already fully described in Chapter XIII, p. 109.

Carbon monoxide. Preparation. Carbon monoxide can be prepared by the reduction of carbon dioxide, by passing the gas slowly through a tube containing red-hot carbon (Fig. 77).

$$CO_2 + C \rightarrow 2CO$$

It can also be prepared by the withdrawal of the elements of water from formic or oxalic acid, although in the latter case the gas is mixed with an equal volume of carbon dioxide. This is best done in each case by heating the acid with concentrated sulphuric acid in a flask, and in the case of oxalic acid passing the mixture of carbon dioxide and monoxide through a strong solution of caustic potash to absorb the carbon dioxide. The carbon monoxide may be collected over a pneumatic trough.

$$\underset{\text{formic acid}}{H_2CO_2} \rightarrow CO + H_2O$$

$$\underset{\text{oxalic acid}}{H_2C_2O_4} \rightarrow CO + CO_2 + H_2O$$

Carbon monoxide is also obtained by the action of strong sulphuric acid (90 per cent. acid) on potassium ferrocyanide, the water of crystallisation in the ferrocyanide, and the water mixed with the acid, taking part in the reaction.

$$K_4Fe(CN)_6, 3H_2O + 6H_2SO_4 + 3H_2O \rightarrow 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO$$

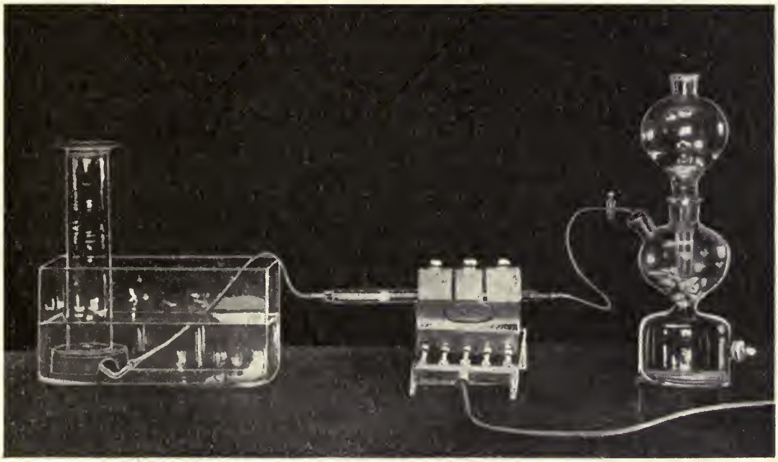


Fig. 77. Preparation of carbon monoxide by passing carbon dioxide over red-hot carbon.

Properties. Carbon monoxide is a colourless, tasteless gas, and has only a faint odour. It is only very slightly soluble in water. It burns in oxygen or air with a pale blue flame forming carbon dioxide, and a mixture of two volumes of carbon monoxide and one volume of oxygen combines with explosive violence, a property which is made use of in gaseous fuels in driving gas engines.

$$\underset{\text{2 vols.}}{2CO} + \underset{\text{1 vol.}}{O_2} \rightarrow \underset{\text{2 vols.}}{2CO_2}$$

Carbon monoxide does not support combustion. It is a good reducing agent, and will reduce metallic oxides, such as copper oxide, to the metallic state, the carbon monoxide being converted into the dioxide.

$$CuO + CO \rightarrow Cu + CO_2$$

If treated with chlorine in bright sunlight an extremely poisonous compound called carbonyl chloride or phosgene is formed, which in small doses affects the heart. This substance is used in the manufacture of dyestuffs.

$$CO + Cl_2 \rightarrow COCl_2$$

Carbon monoxide is itself extremely poisonous, and air containing only 0·1 per cent. will prove poisonous if breathed for any considerable time. It forms a very stable compound with the haemoglobin of the blood, known as carboxy-haemoglobin, and thus renders the revival of persons suffering from carbon monoxide poisoning a difficult operation; carbon monoxide poisoning is easily recognised by the livid appearance of the skin.

Carbon monoxide is formed when a coke or coal fire is burning very red, and is the cause of the blue flame flickering over the top of the fire. In this case carbon dioxide is produced where the carbon first burns in contact with air, and the CO_2 passing over the red-hot coal forms carbon monoxide, which burns with a blue flame forming CO_2 where it again comes into contact with the air at the top of the fire.

Owing to its very poisonous character, it is of the greatest importance to ensure a sufficient supply of air in all coal stoves, gas fires, etc., so as to form carbon dioxide as the final product.

Carbon monoxide is soluble in cuprous chloride, dissolved in ammonia or hydrochloric acid, and this reagent is used in gas analysis to separate it from other gases. The ammonia solution will dissolve about 50 per cent. more of the gas than the acid solution.

Gaseous fuels.

Carbon monoxide is the principal combustible constituent of various forms of gaseous fuels, such as **producer gas, water gas, Dowson** and **suction gases.** These are largely used for heating purposes or for driving gas engines, and in the former case possess the following advantages over solid fuels: (1) the heating of the furnace may be more easily regulated; (2) the gaseous fuel may be given a preliminary heating before being burnt and the final temperature attained in the furnace is consequently higher; (3) the fuel is readily conveyed to any part of the furnace to be heated.

Producer gas. The term producer gas is derived from the fact that the gas is prepared in forms of furnaces known technically as "gas producers." The gas is made by passing air over heated carbon, generally coke or anthracite, at a temperature of approximately 1000° C., the following chemical action taking place:

$$\underset{}{2C} + \underset{\text{1 vol.}}{O_2} \rightarrow \underset{\text{2 vols.}}{2CO}$$

From the above equation it will be seen that 5 vols. of air containing 1 vol. of oxygen will produce 6 vols. of producer gas, containing 4 vols. of nitrogen and 2 vols. of carbon monoxide. This is the ideal composition of the gas, *viz.*, 67 per cent. N and 33 per cent. CO, but in actual practice it is considered a satisfactory result if a gas of the following average composition is obtained: 67 per cent. N, 29 per cent. CO, 4 per cent. CO_2.

It is of the greatest importance to keep the amount of CO_2 as low as possible, since this gas is non-combustible, and the principal conditions to be observed for this purpose are (1) to regulate the amount of air passing into the furnace, (2) to keep the temperature as near to 1000° C. as possible, (3) to employ a good depth of fuel in the furnace, so that any CO_2 formed may be converted into CO by passage over the red-hot carbon, thus:

$$CO_2 + C \rightarrow 2CO$$

At 600° C. the carbon forms principally CO_2 and very little CO, but the percentage of the latter rises with the temperature, until at 1000° C. with proper conditions the average composition mentioned above should be obtained.

The heat produced during the formation of the gaseous fuel, and during the combustion of it, *i.e.*, during its use, are shown in the following thermal equations:

$$\underset{\underbrace{2\,(12)}_{24}}{2C} + O_2 \rightarrow 2CO + 58{,}800 \text{ calories}$$

$$\underset{\underbrace{2\,(12+16)}_{56}}{2CO} + O_2 \rightarrow 2CO_2 + 136{,}400 \text{ calories}$$

These equations show that the combustion of 24 grams of carbon forming producer gas will produce sufficient heat to raise 58,800 grams of water through 1° C. rise of temperature, and the combustion of 56 grams of CO will raise 136,400 grams of water through 1° C., the positive sign (+) being used to indicate the production of heat.

The total heat produced is shown by the sum of the two equations, thus:

$$2C + 2O_2 \rightarrow 2CO_2 + 195{,}200 \text{ calories}$$

Of this total heat, approximately one-third is formed during the production of the producer gas, and only the remaining two-thirds is available for heating purposes, so that apparently for heating purposes it is more advantageous to use solid fuels, but against this loss of heat must be placed the economical use of the gaseous fuel and the advantages which have been already mentioned.

The production of heat in the manufacture of producer gas causes the temperature of the generator or furnace to rise to a point at which the metal parts are melted, and, to prevent this, water is run on to the fire bars of the furnace, thus generating steam which acts on the red-hot carbon with an absorption of heat, this being shown in the equation by the use of a negative sign, thus:

$$C + H_2O \rightarrow H_2 + CO - 28{,}800 \text{ calories}$$

The furnaces are also constructed with a pool of water in the bottom known as "water-bottom producers," and the red-hot ashes or clinker falling into the pan of water similarly generate steam which passes with the air into the furnace.

A modern form of Siemens' gas producer is shown in Fig. 78.

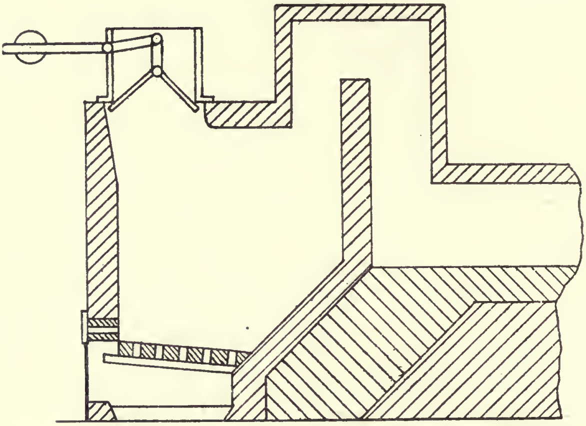


Fig. 78. Siemens' modern gas producer.

Water gas. Water gas is made by passing steam over carbon, either in the form of coke, anthracite, coal or charcoal, the temperature being kept up to 1000° C., as at lower temperatures carbon dioxide is formed and little or no CO is produced at 600° C.

$$\text{At } 1000^\circ \text{ C.} \quad H_2O + C \rightarrow \underbrace{CO + H_2}_{\text{“Water gas”}} - 28{,}800 \text{ calories}$$

$$\text{At } 600^\circ \text{ C.} \quad 2H_2O + C \rightarrow CO_2 + 2H_2 - 18{,}800 \text{ calories}$$

The former equation is made up of the following reactions:

$$H_2O \rightarrow H_2 + O - 58{,}200 \text{ calories}$$
$$C + O \rightarrow CO + 29{,}400 \text{ calories}$$

The equation above for 1000° C. shows that water gas is composed of equal volumes of carbon monoxide and hydrogen, but in actual practice about 5 per cent. of carbon dioxide is usually formed, as indicated in the reaction taking place at 600° C.

As the temperature of the furnace gradually falls through absorption of heat, the percentage of CO_2 produced gradually increases, and the steam is stopped after a time and air admitted. The generators are therefore usually built in duplicate, and whilst air is passing through one steam is being passed through the other. Water gas burns with a blue flame and is often known commercially as "blue water gas." The following is given as an approximately average composition: hydrogen, 50 per cent., carbon monoxide, 42 per cent., carbon dioxide, 4 per cent., methane, etc., 1 per cent., nitrogen, 3 per cent. It is stated that, when burnt, it produces a flame temperature of nearly 3400° F. It is used for welding, brazing, melting, etc., and for the manufacture of hydrogen. It has also been used for lighting purposes in conjunction with incandescent mantles, and as an illuminant when carburetted with petroleum vapour, etc., though its extremely poisonous and odourless character is an objection to its use for lighting purposes.

Dowson gas. Dowson gas is a mixture of water gas and producer gas, with an approximate composition: carbon monoxide, 25 per cent., hydrogen, 20 per cent., carbon dioxide, 5 per cent., nitrogen, 50 per cent. It is obtained by passing high pressure superheated steam into the furnace by means of a suitable tube, so that the steam carries with it through the tube a current of air on the injector principle. By suitably regulating the proportions of steam and air in the mixture, the temperature of the furnace may be kept fairly constant during the working. Fig. 79

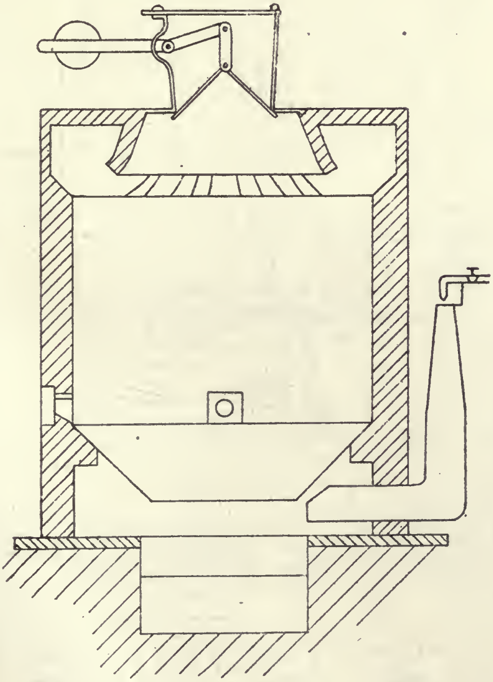


Fig. 79. Dowson water-bottom gas producer.

shows a water-bottom generator of this type in which the Dowson gas, escaping into an annular chamber before being conveyed away from the furnace, is used to give the fuel a preliminary heating.

Suction gas. Suction gas is of a similar composition to Dowson gas, the air and steam being drawn through the generator, as shown in Fig. 80, by the suction stroke of the piston of the gas engine, driven by

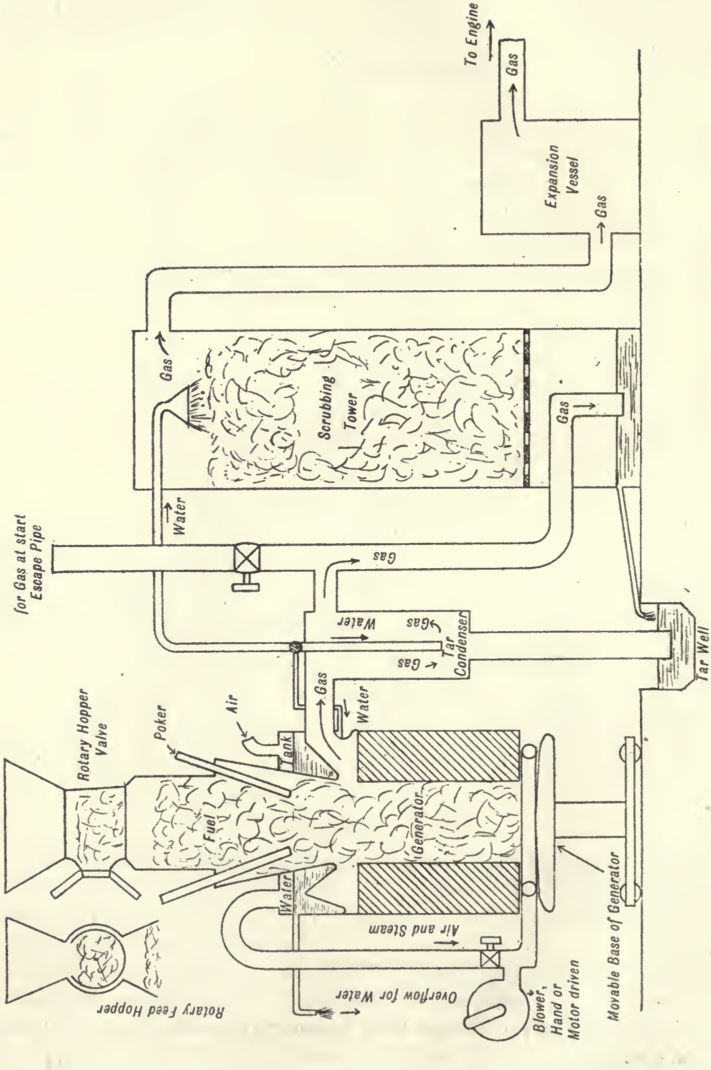


Fig. 80. Crossley suction gas plant.

the explosion of a mixture of suction gas and air. The generator must first be heated either by hand-blowing or by means of a motor or fan, a current of air being driven through the generator. The gas is allowed to escape until the generator is sufficiently raised in temperature, and the gas is then passed through the cooler and scrubbing towers. The latter are filled with coke over which water is falling, so as to remove tar, and the gas then passes mixed with air into the cylinder of the engine. When the engine has been started, the motor and fan may be stopped, and the air is then drawn over a heated water tank, so that a mixture of air and steam passes into the generator.

Combustion and analysis of gases.

When solid fuel is used in a furnace for heating purposes, such as steam-raising, it is important to have a sufficient supply of air to entirely convert the carbon into the dioxide. Any carbon monoxide escaping with

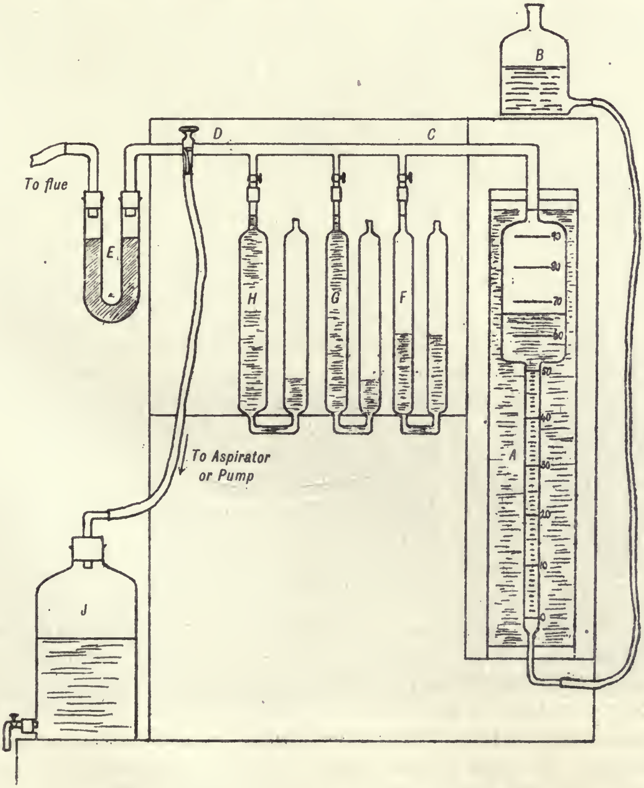


Fig. 81. Orsat's apparatus for analysis of furnace gas.

the furnace gas means a loss of fuel, as it has already been shown that carbon monoxide is a valuable gaseous fuel, and to obtain complete combustion of the carbon an excess of air must be employed. It is considered a satisfactory result if the furnace gas has the following approximate composition: nitrogen, 80 per cent., carbon dioxide, 12 per cent., oxygen, 8 per cent., carbon monoxide, nil. A considerable saving in fuel may be obtained by making regular analyses of the furnace gas, and careful regulation of the combustion in accordance with the analyses obtained, the object being to obtain the maximum quantity of carbon dioxide with the minimum quantity of air, whilst avoiding the escape of carbon monoxide in the furnace gas. In the case of gaseous fuels, too, it is of the greatest importance to keep a continual watch on the composition of the gas, in order to obtain the maximum quantity of combustible gas and maximum heating effect from the use of the fuel.

Analysis of furnace gas: Orsat's apparatus. Orsat's apparatus, which is usually employed for the analysis of furnace gas, is simply a modified and compact form of the Hempel apparatus. The apparatus is shown diagrammatically in Fig. 81, and a photograph is shown in Fig. 82. The burette, *A*, is surrounded by a cold water jacket, and is connected below to the pressure bottle, *B*, whilst the top part is attached to the capillary tube, *C*. The latter is provided with several branch tubes, and a three-way tap, *D*, whilst the end of the tube, *C*, is attached to the filter tube, *E*, containing cotton wool for filtering out grit from the furnace gas. The branch tubes are attached to pipettes, *F*, *G*, and *H*, which contain respectively caustic potash for absorption of CO_2, an alkaline pyrogallic acid solution for absorption of oxygen, and an ammoniacal cuprous chloride solution for absorption of carbon monoxide.

In using the apparatus, the pipettes are first filled with solutions up to the mark on each of the connecting tubes, and any gas in the burette is driven out through the three-way tap by raising the pressure bottle, the burette being filled to the mark. By means of the aspirator, *J*, furnace gas is drawn off through a tube from the gas flue until all the air has been displaced from the filter tube, *E*, the tap, *D*, being turned into a suitable position to put *J* and *E* into communication whilst cutting off connection with the burette. The tap, *D*, is then turned to put the tube, *E*, and the burette, *A*, into communication, and 100 c.c. of furnace gas are drawn into the burette by lowering the bottle, *B*. The level of the liquid in the bottle, *B*, is arranged at the same height as the level of liquid at the zero mark on the burette, and the tap, *D*, is turned to cut off the burette from the tube, *E*, and the aspirator, *J*.

100 c.c. of furnace gas have thus been measured at the temperature of the water bath, and under the barometric pressure at the time of the experiment. The gas is now passed into the potash pipette by raising the bottle, *B*, and opening the tap communicating with the pipette, *F*,

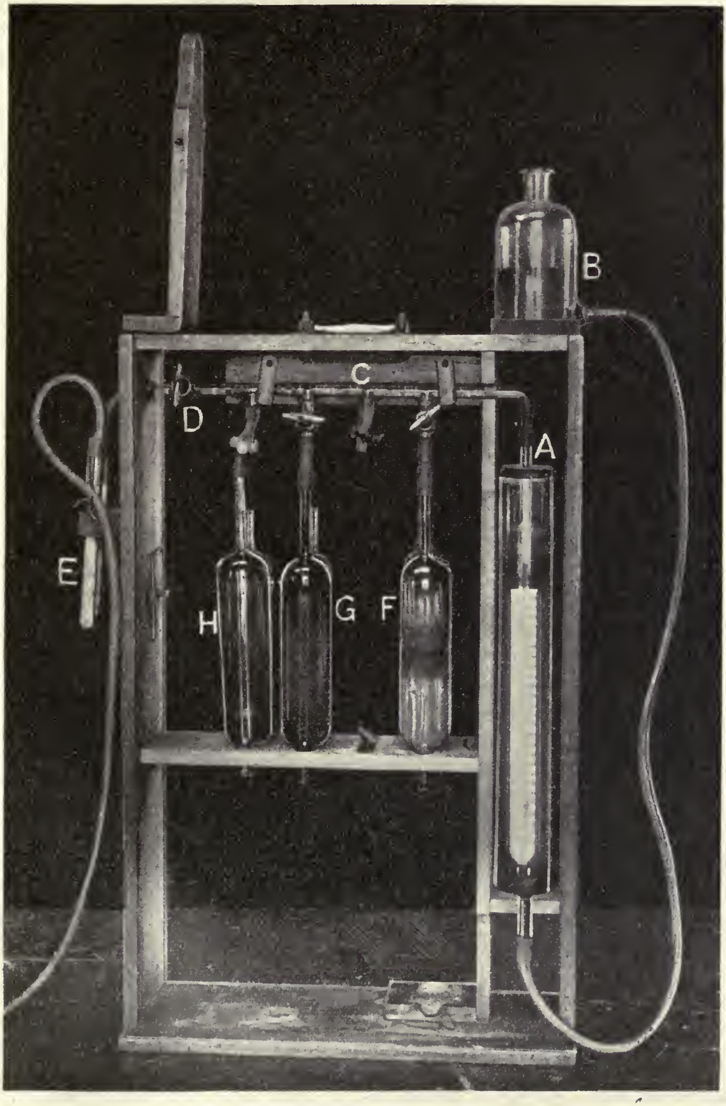


Fig. 82. Orsat's apparatus for the analysis of furnace gas.

the gas being left for a few minutes in contact with the solution of potash. It is then drawn back into the burette until the potash is at the mark on the pipette, the tap closed, and the gas again measured at the pressure of the atmosphere by adjusting the height of the bottle, *B*. This is repeated until there is no further diminution in volume, and the loss in volume, read off directly on the burette, gives the percentage of CO_2.

The percentages of O and CO are obtained in a similar manner by passing the gas successively into the "pyro" pipette, and the cuprous chloride pipette, all the readings of volumes being taken at atmospheric pressure.

The preparation of the potash and "pyro" solutions has been already described (see Chapter XVI, p. 142). The ammoniacal cuprous chloride solution is prepared by heating 10 grams of CuO in 200 c.c. conc. HCl and metallic copper turnings till nearly colourless, and then pouring the cuprous solution into about 1 litre of water. The cuprous chloride is settled, the clear liquor poured off, about 175 c.c. of water added and ammonia led into the liquid until the cuprous chloride is dissolved forming a blue solution. The cuprous chloride may be dissolved in HCl instead of NH_3, but the absorptive power of the alkaline solution is greater than the acid one.

Silicon: Symbol, Si; atomic weight, 28.

With the exception of oxygen, silicon is the most abundant element occurring in the earth's crust. It always occurs in combination with other elements, and mainly with oxygen, with which it forms a dioxide similar in constitution and chemical properties to carbon dioxide. In fact carbon and silicon in many ways show a similarity in allotropic forms and in the compounds which they form.

The element may be liberated from its oxide by heating the finely powdered oxide with magnesium powder.

$$SiO_2 + 2Mg \rightarrow 2MgO + Si$$

Silicon is a brown amorphous powder and on heating will burn readily in air or oxygen. By fusing the silicon with aluminium and allowing the melt to cool, the silicon may be obtained in the form of hard crystals by treatment with acids to dissolve the aluminium. It is also produced in the electric furnace by reducing sand by means of coke, and is prepared for manufacturing ferro-silicons for various purposes, such as acid-resisting metal.

Silica. The chief source of silicon is silica, or silicon dioxide, SiO_2, and this occurs in many forms, the most abundant being quartz, sand, sandstone, flint, kieselguhr and agate.

Quartz occurs as large six-sided prisms generally capped by pyramids, and very commonly in igneous rocks, granite consisting of quartz associated with felspar and mica.

Sand and **sandstone** probably give rise to the largest amount of silica, sandstone consisting of grains of sand held together by other substances, the cementing material being generally also silica.

Kieselguhr is a powder, consisting of the skeleton remains of diatoms, which are lowly forms of plants found in water. It has the power of absorbing liquids such as nitroglycerine, and is used in the manufacture of dynamite.

Pure silica. Pure silica may be prepared from any of the natural forms, either the free forms as sandstone, or the complex minerals known as silicates, such as felspars, micas, etc., found in igneous rocks. The powdered material is intimately mixed with several times its weight of sodium or potassium carbonates, or a molecular mixture of these (fusion mixture), and the whole fused until the evolution of gas ceases and a clear melt is obtained. The alkaline silicate is then dissolved, and decomposed by the addition of dilute hydrochloric acid, the sodium chloride remaining in solution :

$$Na_2SiO_3 + 2HCl \rightarrow 2NaCl + H_2SiO_3$$

The gelatinous silicic acid, H_2SiO_3, is filtered off, dried and heated to form SiO_2.

One of the chief uses of silica is for the manufacture of **quartz glass** or fused **silica ware.** Silica melts at a very high temperature only (about 1700° C.); its production as silica ware has been rendered possible only with the high temperatures which have been obtained by the aid of the electric furnace. The coefficient of expansion of this material is extremely low, and it is not affected in structure by very sudden changes of temperature. For example, cold water may be poured into a white-hot silica vessel without cracking it or in any way damaging it.

This material has found very useful applications in recent years, in the production of laboratory vessels for special purposes, vessels for the manufacture of nitric acid, concentration vessels in the manufacture of sulphuric acid (see Chapter XIX, p. 191), etc.

Silicic acids and silicates. Silicic acid may be obtained in probably several forms, the two most important being **metasilicic acid, H_2SiO_3**, and **orthosilicic acid, H_4SiO_4.** The former is produced as a gelatinous precipitate by adding dilute hydrochloric acid to a solution of sodium silicate as already described, whilst the ortho-acid, H_4SiO_4, is produced in solution by adding a solution of sodium silicate to an excess of dilute hydrochloric acid.

$$Na_2SiO_3 + 2HCl + H_2O \rightarrow H_4SiO_4 + 2NaCl$$

Dialysis : Colloids and crystalloids. Graham showed in 1861 that crystalline substances in solution readily passed through a parchment membrane into water, whilst other bodies, such as gelatine or glue, did not diffuse readily, and these latter bodies he termed colloids. This process of diffusion, which he termed dialysis, may be made use of for separating colloids, such as gelatine or silicic acid, from crystalline substances, termed crystalloids when in solution. The dialyser consists of a hoop or cylindrical cell of wood or gutta percha covered with parchment or pig's bladder, and the solution to be dialysed is placed in this and floated in water which is renewed from time to time. The crystalline body diffuses through the parchment into the water, whilst the colloid is mostly retained in the dialyser.

It has been definitely proved that the colloids are aggregations of molecules, and the multi-molecules can be in some cases seen in a perfectly clear solution when viewed in a special instrument known as the **ultra-microscope.**

The colloidal condition may take two forms, the **sol** condition when in the fluid form, and the **gel** condition when gelatinous. If dissolved in water these forms are known as the **hydrosol** and the **hydrogel** conditions. Many bodies such as starch, glue, gelatine, gums, silicic acid, ferric and aluminium hydroxides, and other gelatinous bodies, may take both the hydrosol and the hydrogel conditions. The colloidal condition and the properties of the colloidal solutions appear to be intimately bound up with the various life processes in living matter, and many of the actions in dyeing operations may also possibly be of a colloidal character.

The silicic acid obtained in the above preparation may be separated from the sodium chloride, and thus obtained in the pure state by this process of dialysis. The solution containing both substances is placed in the dialyser, and the cell is then placed in pure water, so that the level of the liquid is the same inside and outside. The sodium chloride passes through the membrane into the water until the strength of the sodium chloride is the same on either side of the membrane. If fresh water is then placed on the outside, a further quantity of salt will pass through and the process can be repeated until all the sodium chloride has been removed. The hydrosol solution of orthosilicic acid remaining is, however, very unstable, and if concentrated beyond about 15 per cent. it passes into the insoluble gelatinous or hydrogel condition (H_2SiO_3).

Sodium silicate. Sodium silicate is obtained by fusing a mixture of powdered quartz and soda ash in a furnace. The melt is allowed to cool, broken up and then extracted with water. The composition varies considerably, but may be regarded commonly as sodium silicate, Na_2SiO_3. It is usually met with in commerce as a syrupy liquid, and is also known under the name of **water glass**, since it is soluble in water and on evaporation the solution gives a clear glass.

Sodium silicate is slowly decomposed by carbon dioxide, silica being deposited and sodium carbonate formed.

It is used for the manufacture of artificial stone, for weighting soap, for fireproofing, for fireproof cement, and for printing and bleaching textiles.

Kaolin (China clay). Kaolin is found in England in large quantities in Cornwall, and is essentially a silicate of alumina ; it may be represented by the formula, Al_2O_3, $2SiO_2$, $2H_2O$. It forms a pure white clay, and ordinary clays are similar in composition but are coloured by impurities. Kaolin is formed from minerals contained in igneous rocks, such as felspars, by a process of **kaolinisation.** These minerals consist mostly of complex silicates of aluminium and the alkali metals, potassium and sodium, or the alkaline earths, such as calcium or magnesium. By the slow and continued action of natural water containing carbonic acid in solution, the alkalis and alkaline earth metals are removed in solution as soluble bicarbonates, ultimately leaving a pure white clay known as kaolin. Granite may thus gradually pass into kaolin, which is soft enough to be dug out by a spade.

It is used in the production of pottery, the best forms of china and porcelain, and is also used in textile operations in the weighting of materials, giving a soft handle to textile fabrics.

Carborundum. Carborundum or silicon carbide, SiC, is made by heating together sand, coke, sawdust, and a small quantity of sodium chloride in an electric furnace. Very heavy currents are used between graphite electrodes.

$$SiO_2+3C \rightarrow SiC+2CO$$

It is obtained as bright greenish crystals which are extremely hard and very resistant to acids. On account of its hardness it is used to a large extent for polishing stone and metals, and as a substitute for emery in the grinding and sharpening of engineering tools.

PART III

CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES (ORGANIC CHEMISTRY)

(DEALING PRINCIPALLY WITH THOSE COMPOUNDS OF IMPORTANCE IN THE TEXTILE INDUSTRIES)

CHAPTER XXI

PRELIMINARY

APPROXIMATE ANALYSIS: FRACTIONAL DISTILLATION: QUALITATIVE ANALYSIS: QUANTITATIVE ANALYSIS: EMPIRICAL AND MOLECULAR FORMULAE, VAPOUR DENSITY AND MOLECULAR WEIGHT.

Organic chemistry. The study of the compounds of carbon, so far as they relate to the hydrocarbons and their derivatives, is dealt with under the title "organic chemistry," though there is actually no sharp line of demarcation between inorganic and organic chemistry.

Various modes of classification have been used in past years, such as the classing of mineral bodies, or substances found in the mineral kingdom, as "inorganic"; whilst substances found in the animal or vegetable kingdom, and supposed to be formed by the agency of "vital force," were termed "organic bodies," from the fact that they occurred in organised forms of life or bodies with organs.

All such modes of classification have, however, broken down, and a very great number of substances occurring naturally in forms of life may now be produced artificially in the chemical laboratory from mineral bodies. The production of urea from ammonium cyanate by Wöhler in 1828 was the first synthesis of a body known up to that time only in forms of life, and this discovery broke down the theories held at that time with regard to organic and inorganic substances.

Certain substances, *e.g.*, the allotropic varieties of carbon, the oxides of carbon, carbonic acid and carbonates, are commonly dealt with amongst inorganic substances, and the study of the hydrocarbons and their derivatives is now commonly termed "organic chemistry."

Reasons for the separate study. There are many reasons for studying these bodies separately, but the principal ones are: (1) the great number of compounds known; (2) absolutely different compounds frequently contain the same number and character in their atoms; (3) the atoms are often found in groups conferring particular properties on the substances.

Elements present in organic compounds. The elements commonly present are very few in number. Carbon is essential and hydrogen is nearly always present. The halogens, Cl, Br, and I, may replace H. Oxygen is a common element, and the three elements, C, H, and O, form by far the greater number of compounds, such as alcohols, ethers, acids, salts, etc. Nitrogen and sulphur are less commonly found, whilst P, As, and the metals are much more rare.

Analysis and recognition of organic compounds. In almost all cases when an organic substance is produced, it is formed in an impure state, and before it can be recognised and classed it must be analysed as follows: (1) by approximate analysis, the body is purified; (2) by qualitative analysis, the elements are detected; (3) by quantitative analysis, the percentages of the elements are obtained.

The simplest or empirical formula may then be deduced, and from determinations of the molecular weight of the substance the molecular formula may be obtained. From its mode of preparation, or from its properties or reactions, information may be obtained regarding the arrangement of the atoms in the molecule, that is, a knowledge may be obtained of the constitution or structural formula of the substance, and finally, by suitable reactions, the body may be classed as an alcohol, ether, acid, etc.

Approximate analysis—purification of solids. If the substance is a solid it may be dissolved in suitable solvents and then crystallised. By separating the crystals in fractions during the process of crystallisation portions differing in purity may be obtained, a process known as **fractional crystallisation.**

Fractional solution, in which one takes advantage of the different degrees of solubilities of the substance and its impurity in small quantities of reagent, may also be employed, and also **fractional precipitation** by gradual addition of reagents. The solvents commonly used are water, alcohol, ether, benzene, chloroform, acetic acid, acetone, etc.

When a substance is in solution in one solvent, it may sometimes be **extracted by** a second **solvent** and the two liquids separated by making use of a stoppered funnel, and in certain cases may be separated from impurities in this way.

Thus, if a solution of alizarin in acetic acid is shaken up with ether, the lighter ethereal layer will afterwards separate with the alizarin in solution.

It is only by variations and combinations of these processes, decided upon after trial, that a body can be obtained in a pure state.

The purity is decided in the case of a solid by the **melting point (M.P.),** the body melting completely at a definite temperature, or within 1° or 2° C. if pure, and the melting point is then said to be "sharp." Impurities tend to lower the M.P., and cause the body to melt through several degrees rise in temperature **(Range of M.P.).**

The melting point is determined by enclosing a small quantity of powder in a thin-walled capillary tube, sealed at one end, and attached to the bulb of a thermometer, so that the substance lies alongside the bulb. The bulb and substance are immersed in a bath of water, concentrated sulphuric acid, or melted paraffin wax, which is heated very gently so as to raise the temperature slowly. When melting commences, the temperature is kept steady until no further change takes place, and the temperature is then slowly raised 1°, this being continued progressively until the whole of the substance is melted. Determine the melting point of naphthalene (80° C.).

Purification of liquids—fractional distillation. If the body is a liquid, the boiling point is taken as a criterion of purity, and is obtained by distilling the liquid as shown in Fig. 19 (see p. 31), a distilling flask with a side tube low on the neck being used for high boiling point liquids, and with a side tube high on the neck for low boiling point liquids.

The process of fractional distillation is carried out by distilling the liquid and collecting in several fractions at approximately equal intervals of temperature, the several fractions being numbered. Thus, with a mixture of alcohol (B.P. 78° C.) and water (B.P. 100° C.), the liquid will distil continuously between these limits, the portion distilling nearer to 78° C. being richer in alcohol, and nearer to 100° C. richer in water. The following fractions may be collected: Frac. (1), 78°—83°; Frac. (2), 83°—88°; Frac. (3), 88°—90°; Frac. (4), 90°—95°; Frac. (5), 95°—100° C.

Fraction (1) is then replaced in the flask, distilled, and the portion distilling between 78°—83° C. collected in the flask labelled Frac. (1). At 83° C., the distillation is stopped and Frac. (2) added to the residue in the distilling flask. Distillation is recommenced, and portions distilling between 78°—83° C. collected in Frac. (1) flask, and between 83°—88° C. in Frac. (2) flask. Each fraction is treated in a similar manner. When each fraction has been distilled, the process is repeated until the fractions (2), (3), and (4) disappear, the distillate ultimately collecting round the two boiling points 78° C. and 100° C., and separating into two practically pure liquids.

In actual practice, for separating mixtures of liquids, fractional still heads (deflagmators) are used, and these are connected to an ordinary flask and condenser, as shown in Fig. 83, the operation being a single and continuous one.

The still heads may be divided into two classes:

(1) Those which offer a large condensing surface to the vapour, thus condensing the higher B.P. liquid and allowing the lower B.P. liquid to pass over. Several of these are shown in Fig. 84.

(2) Those which condense the vapour into several fractions, the number depending upon the construction of the apparatus. Some forms are shown in Fig. 85.

Fractionating columns used in commerce depend upon a similar principle, and one form is shown in Fig. 86. The fractions will have different compositions, and each condensed fraction travels downwards to the

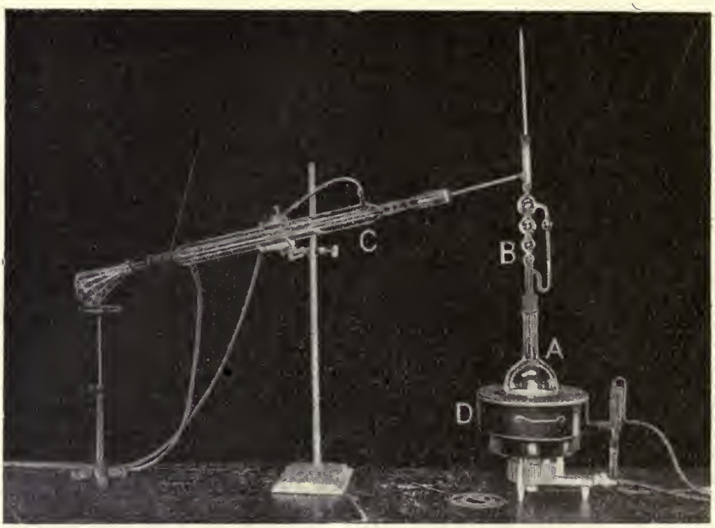


Fig. 83. Use of a fractional still head in separating two liquids by fractional distillation. *A*, flask; *B*, Glynsky still head; *C*, condenser; *D*, water bath.

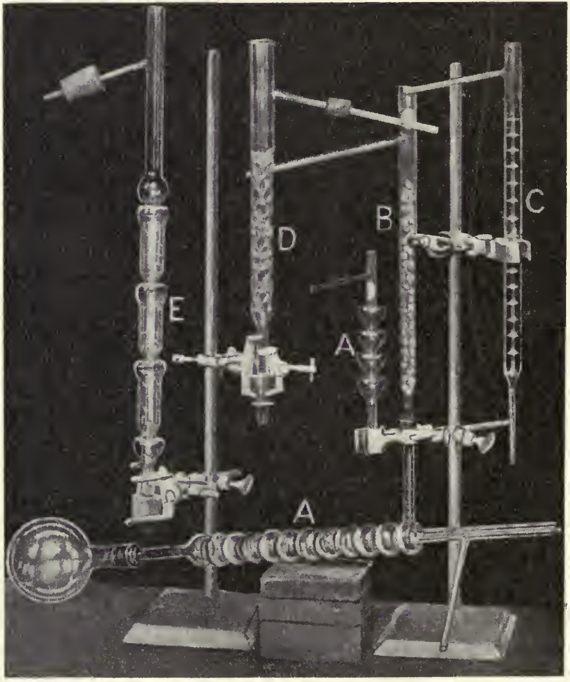


Fig. 84. Fractional still heads, offering a large cooling and condensing surface to the vapour. *A*, pear-shape still head; *B*, Hempel form; *C*, rod and disc; *D*, Vigreux form; *E*, Young and Thomas form.

fraction of higher B.P., the lowest B.P. fraction only passing over as vapour into the condenser.

Qualitative analysis. The qualitative analysis of organic bodies consists in the detection of the elements present, principally those which are dealt with below.

Detection of carbon and hydrogen. Carbon may in some cases be detected by the charring produced (*a*) by heating on platinum foil, (*b*) by heating with concentrated sulphuric acid in a test tube.

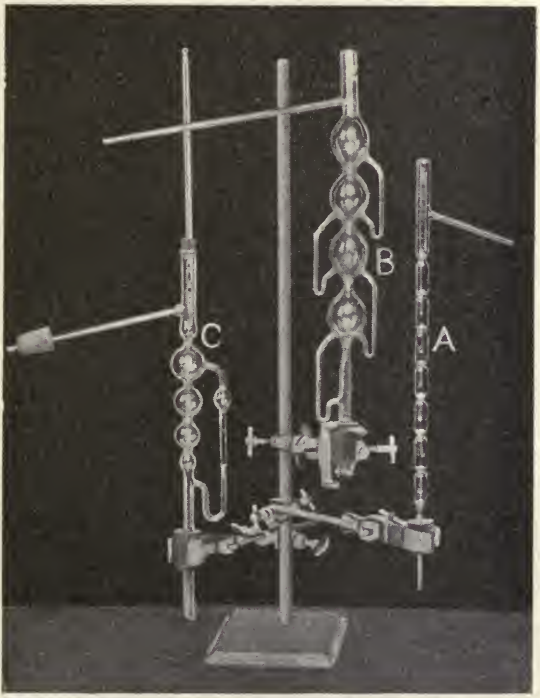


Fig. 85. Fractional still heads separating the condensing liquid into several fractions. *A*, Young and Thomas platinum gauze cone; *B*, Le Bel and Henninger; *C*, Glynsky.

A better method is to heat the substance with granular copper oxide, as in Fig. 87, the evolved carbon dioxide being detected by lime water (showing presence of C), and the water (showing presence of H) by the blue colour formed with grey anhydrous copper sulphate.

Detection of halogens, nitrogen, and sulphur. A small piece of sodium is cut into thin threads, and mixed with the powdered substance in a small ignition tube, and heated *gradually* to a red heat. Whilst hot it is dropped into water, and the liquid filtered. The filtrate is tested:

(*a*) **For halogens.** Nitric acid is added and gently warmed to decompose cyanides and neutralise caustic soda, and silver nitrate added. A white, yellow white, or yellow precipitate indicates chlorine, bromine, or iodine respectively.

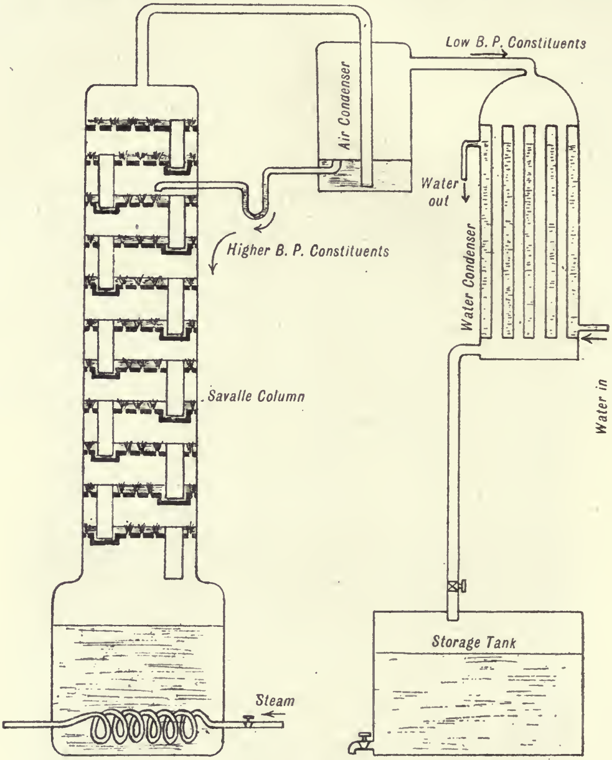


Fig. 86. Fractional distillation.—Savalle still head.

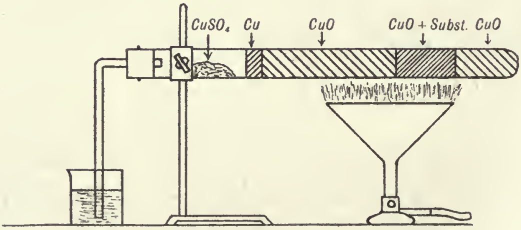


Fig. 87. Detection of carbon and hydrogen.

A small portion of the liquid is evaporated to dryness and the residue heated with MnO_2 and dilute H_2SO_4. A green, brown, or violet gas indicates chlorine, bromine, or iodine respectively.

(*b*) **For nitrogen.** Potassium cyanide will be present in the liquid if N is present, and the filtrate is added in excess to 1 or 2 drops of a freshly-made solution of ferrous sulphate, a drop of ferric chloride added and dilute HCl. The liquid is then heated, a Prussian blue coloration indicating the presence of N.

(*c*) **For sulphur.** Sodium sulphide is produced in the presence of S, and may be detected by (1) the blackening of a silver coin; (2) the formation of a deep purple coloration on the addition of a freshly-prepared solution of sodium nitroprusside; (3) the formation of a black precipitate by the addition of acetic acid and lead acetate.

Quantitative analysis. This branch of analysis consists in the estimation of the percentages of carbon, hydrogen, halogens, nitrogen, sulphur, etc.

Estimation of carbon and hydrogen. A weighed quantity of substance is heated in a current of air or oxygen, so as to completely convert the carbon and hydrogen into carbon dioxide and water respectively. The gas is passed over red-hot copper oxide to convert any CO into CO_2, and the latter is absorbed in weighed bulbs containing caustic potash solution, whilst the water is absorbed in a weighed calcium chloride tube. From the weights of carbon dioxide and water obtained, the percentages of carbon and hydrogen may be calculated.

Estimation of nitrogen. The nitrogen may be estimated by heating a weighed quantity of the substance in a combustion tube with copper oxide, and the gases evolved are passed into a burette containing caustic potash to absorb the CO_2. From the volume of N obtained, corrected to standard temperature and pressure, its weight may be calculated and the percentage of N.

The nitrogen may also be estimated by heating a weighed quantity of substance with soda lime, the evolved ammonia being passed into a measured quantity of N/1 acid. By titrating the remaining acid with standard alkali, the amount of NH_3 evolved, and therefore the percentage of N, may be calculated.

Kjeldahl's method of estimating the nitrogen in textile waste. The estimation of N in organic compounds is most frequently carried out by this method, and it may be also applied successfully to the determination of N in wool fibres, in estimating the value of certain waste textile products for manuring purposes, *e.g.*, the dust from singeing, cropping, etc.

A weighed quantity of the substance is heated with concentrated H_2SO_4 (about 20 c c.) in a round-bottom flask, supported in an inclined position, until charring is complete, and finally about 8 grams of K_2SO_4 together with a little $CuSO_4$ are added, the heating being continued until the liquid becomes clear.

The acid is carefully poured into about 150 c.c. of a 30 per cent. solution of KOH in a litre flask, and steam is blown through the liquid for about 45 to 60 minutes, as shown in Fig. 88. The steam and ammonia gas liberated are passed through the condenser, which delivers into a measured quantity (50 c.c.) of N/1 H_2SO_4. The excess of acid is titrated with N/1 NaOH, using methyl orange as indicator, and the percentage of N is calculated.

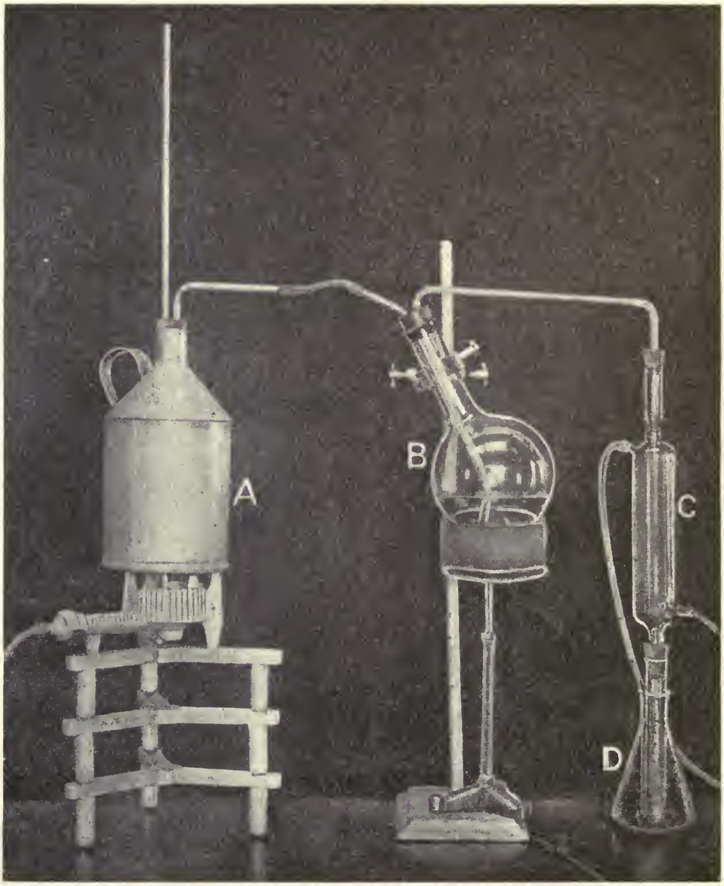


Fig. 88. Estimation of N in organic compounds, for example in wool waste, by the Kjeldahl process. The process shows also the method of steam distillation, *e.g.*, in distilling such substances as aniline oil in steam. *A*, steam can; *B*, flask containing alkali; *C*, condenser; *D*, flask containing N/1 H_2SO_4.

Example.

2 grams of wool taken.

50 c.c. of $\frac{N}{1}$ H_2SO_4 employed.

26·7 c.c. of $\frac{N}{1}$ NaOH used in the titration = 26·7 c.c. $\frac{N}{1}$ H_2SO_4.

Amount of $\frac{N}{1}$ H_2SO_4 neutralised by NH_3 = 50 − 26·7 = 23·3 c.c.

1 c.c. $\frac{N}{1}$ H_2SO_4 = 0·017 gram NH_3 = 0·014 gram N.

2 grams of wool contain 23·3 × 0·014 gram N.

100 „ „ „ $\frac{23{\cdot}3 \times 0{\cdot}014 \times 100}{2} = 16{\cdot}3$ grams

= 16·3 per cent. N.

Estimation of halogens, sulphur, and phosphorus. These elements are estimated by heating with fuming nitric acid to about 200°—250° C. in a sealed tube, placed in a protecting iron tube in an air bath. If a halogen is to be estimated, a small quantity of solid silver nitrate is put into the sealed tube with the acid, silver chloride, bromide, or iodide being formed, which is afterwards washed, dried, and weighed. In the case of sulphur and phosphorus, sulphuric and phosphoric acids are formed, and from these acids compounds of definite composition, such as barium sulphate, are produced, which may be washed, dried, and weighed. From the weight of barium sulphate obtained from a definite weight of the organic substance the percentage of sulphur may be calculated. The phosphorus is estimated similarly.

Percentage of oxygen. When the percentages of all the elements have been obtained, the figures are added together, and the difference of the sum of these and 100 will give the percentage of oxygen. There is no direct method of getting the percentage of this element, which is thus always obtained by difference.

Empirical formula. The simplest formula of the body may be obtained by dividing the percentage of each element by the atomic weight of that element, thus obtaining a series of figures representing the ratio of the number of atoms in the molecule.

Example. Acetic acid, 40 per cent. of C, 53·33 per cent. of O, 6·66 per cent. of H.

$$C = \frac{40}{12} = 3{\cdot}33; \quad O = \frac{53{\cdot}33}{16} = 3{\cdot}33; \quad H = \frac{6{\cdot}66}{1} = 6{\cdot}66.$$

These figures are in the proportion:

$$C : H : O = 3{\cdot}33 : 6{\cdot}66 : 3{\cdot}33 = 1 : 2 : 1.$$

Formula is CH_2O.

Molecular formula. Many very different bodies may have the same empirical formula, but have a different molecular formula, *e.g.*,

Name	Empirical formula	Molecular formula	Molecular weight
Formaldehyde	CH_2O	CH_2O	30
Acetic acid	CH_2O	$C_2H_4O_2$	60
Glucose	CH_2O	$C_6H_{12}O_6$	180

The true molecular formula may thus be obtained by finding the approximate molecular weight by experimental methods.

Chemical methods of determining molecular weight. In the case of most acids, the silver salt may be prepared, and a weighed quantity ignited; metallic silver is thus formed, which is weighed. A calculation may then be made, giving the weight of the silver salt which will produce the atomic weight of silver (108) in the case of a monobasic acid, 2 × 108 in the case of a dibasic acid, and so on. This weight of silver salt is its molecular weight, and by replacing in the molecular weight 1 part by weight of H for each 108 parts by weight of silver the molecular weight of the acid is obtained.

A somewhat similar method is used with organic bases, a platinum salt being formed in this case.

Physical methods of determining molecular weight—vapour density. The vapour density method is most commonly employed for the determination of molecular weight, as most organic bodies may be more or less readily vaporised without decomposition, and from the relationship, M.W. = 2 V.D., an approximate determination is obtained.

The most suitable method is **Victor Meyer's,** in which a known weight of organic substance is vaporised (in Victor Meyer's vapour density apparatus), the temperature being kept constant during vaporisation, and the volume of displaced air is obtained at the temperature and pressure of the atmosphere of the room. The volume is reduced to N.T.P., and the weight of 1 c.c. of the vapour of the substance at N.T.P. is thus easily calculated. This weight is divided by the weight of 1 c.c. of H at N.T.P. (0·0000896 gram) in order to obtain the vapour density.

Raoult's method. This may be used for bodies which cannot be vaporised without decomposition, and depends on the amount of lowering of the freezing point, or the raising of the B.P., of a solvent. Thus the molecular weight of a body in grams will lower the freezing point of 100 grams of the solvent by a constant amount = K (acetic acid = 39). As this is only accurate with very dilute solutions, the lowering of the F.P. must be accurately taken by a sensitive thermometer reading to 1/100 of a degree, and a calculation may then be made of the approximate molecular weight.

CHAPTER XXII

HYDROCARBONS OF THE PARAFFIN SERIES

HYDROCARBONS: HOMOLOGOUS SERIES: ISOMERISM: CONSTITUTIONAL FORMULAE: SUBSTITUTION: METHANE AND ETHANE: PETROLEUM: LUBRICATING OILS: PARAFFIN WAX: OILS USED IN THE TEXTILE INDUSTRY.

Hydrocarbons.

Hydrocarbons from petroleum. The mineral product, known as petroleum, consists of a complex mixture of compounds, containing carbon and hydrogen, these compounds being known as hydrocarbons. The simplest of these, methane, CH_4, ethane, C_2H_6, propane, C_3H_8, and butane, C_4H_{10}, are gases at the ordinary temperature of the air, and consequently escape in the gas given off from petroleum wells or springs, whilst the more complex bodies are liquids or solids contained in the liquid petroleum.

The following individual compounds may be either separated from petroleum, or may be obtained by a separate mode of preparation in the laboratory.

Hydro-carbon	Number known.	Formula	Gas, liquid or solid	Boiling point	Sp. gr.	Commercial product
Methane	1	CH_4	gas	− 164° C.	·415 at B.P.	Gas escaping from petroleum wells, fire damp, etc.
Ethane	1	C_2H_6	,,	− 84°	·446 at 0°C.	
Propane	1	C_3H_8	,,	− 37°	·536	
Butane	2	C_4H_{10}	,,	+ 1°	·600	
Pentane	3	C_5H_{12}	liquid	36°	·633 at 15°	Petrol, petroleum ether, paraffin oil and (higher B.P.) light and heavy lubricating oils.
Hexane	5	C_6H_{14}	,,	69°	·658 at 20°	
Heptane		C_7H_{16}	,,	98°	·683	
Octane		C_8H_{18}	,,	125°	·702	
Nonane		C_9H_{20}	,,	150°	·718	
		etc. to				
		$C_{16}H_{34}$	,,	287°	·775	
		$C_{17}H_{36}$	solid			Vaseline. Solid = paraffin wax.
	and higher compounds					

Adjacent members of the series differ by a constant amount, CH_2, and such a series is named a **homologous series.** From the inertness of the particular series of hydrocarbons shown above, these compounds are named **paraffins** or **paraffin hydrocarbons.**

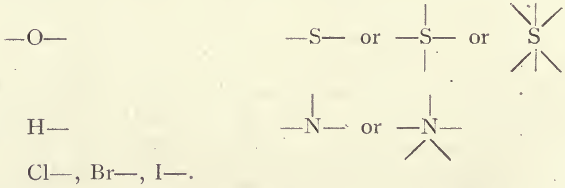
Isomerism. It will be observed from the table above, that there are two compounds known as butane which have been prepared and both have the same molecular formula. The compounds are, however, quite distinct in all their properties, physical and chemical, and are absolutely distinct bodies.

This property is termed isomerism, and bodies having the same molecular formula, but differing in properties, are said to be isomeric. There are various types of isomerism, but the above general definition may for the present be accepted as the definition of isomerism.

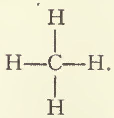
Constitutional or structural formulae. Isomerism can only be explained on the assumption that the arrangement of the atoms in the molecules is different in isomeric bodies, although the number and character of the atoms are the same.

This difference in the structure is shown symbolically by formulae, termed structural or constitutional formulae, which are derived or evolved from a knowledge of the properties and the mode of preparation of the substance, and from the valencies of the atoms in the molecule.

Valencies of atoms in organic bodies. The valencies of atoms in organic compounds are, as a rule, constant, and for the present purpose it may be accepted that carbon is always tetravalent, or is a tetrad, represented symbolically thus $-\overset{|}{\underset{|}{C}}-$; oxygen, a diad; hydrogen and halogens, monads; nitrogen, a triad or pentad; sulphur, a diad, tetrad, or hexad, thus:



There is only one possible way of writing the structural formula of methane, CH_4, so as to satisfy the valency of each atom, *viz.*,

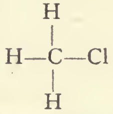


$$H-\overset{\displaystyle H}{\overset{|}{\underset{\underset{\displaystyle H}{|}}{C}}}-H.$$

Substitution. Although it has been mentioned that the general characteristic of these hydrocarbons is their inertness, yet they may be attacked by the action of the halogens ; thus, methane and chlorine, when mixed in equal volumes, react on exposure to sunlight, thus :

$$CH_4 + Cl_2 \rightarrow \underset{\text{methyl chloride}}{CH_3Cl} + HCl$$

From the equation, it will be noticed that an atom of H is withdrawn from the molecule of methane, and an atom of chlorine takes its place ; this can only be done in one way, as all the atoms of H are symmetrically disposed :



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & — & C & — & Cl \\ & & | & & \\ & & H & & \end{array}$$

The action is known as **substitution,** and hydrogen must be withdrawn in order to introduce another atom such as a halogen. By combining this action with a second, in which sodium acts upon methyl chloride, we may pass from methane to ethane, thus :

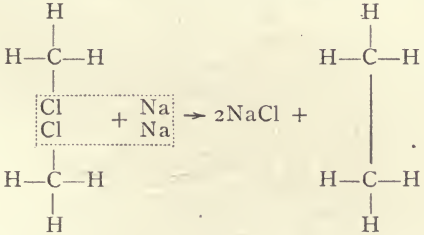
$$2CH_3Cl + 2Na \rightarrow 2NaCl + (CH_3)_2 \text{ or } C_2H_6$$

This latter action is similar to the action of sodium on hydrochloric acid :

$$2HCl + 2Na \rightarrow 2NaCl + H_2$$

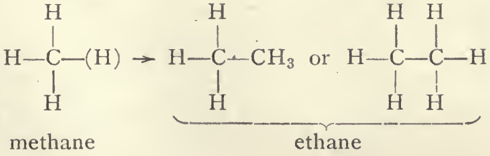
In the latter case the molecule of hydrogen is formed by the chemical combination of two atoms of hydrogen liberated from two molecules of hydrochloric acid, and in the production of ethane it appears to be a similar action, the ethane being formed by the combination of two —CH_3 groups, known as **methyl,** both of which are monad groups, liberated from two molecules of methyl chloride.

The action may be expressed by the following structural equation :



$$\begin{array}{ccc} H & & H \\ | & & | \\ H—C—H & & H—C—H \\ | & & | \\ \boxed{\begin{array}{lcr} Cl & + & Na \\ Cl & & Na \end{array}} & \rightarrow 2NaCl + & | \\ | & & | \\ H—C—H & & H—C—H \\ | & & | \\ H & & H \end{array}$$

The formation of the ethane formula is thus only a substitution of a methyl group CH_3— in place of one atom of hydrogen, represented (H) in the formula of methane.

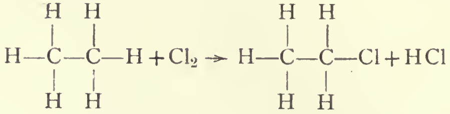


$$\underset{\text{methane}}{\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & — & C & — & (H) \\ & & | & & \\ & & H & & \end{array}} \rightarrow \underbrace{\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & — & C & \leftarrow & CH_3 \\ & & | & & \\ & & H & & \end{array} \text{ or } \begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & H & & H & & \end{array}}_{\text{ethane}}$$

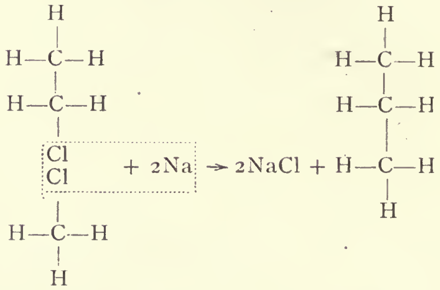
This process may be repeated indefinitely in order to pass from one hydrocarbon to the next higher in the series, thus we may pass from ethane to propane :

$$C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$$
$$C_2H_5Cl + CH_3Cl + 2Na \rightarrow 2NaCl + C_3H_8$$

If these equations are written structurally, the substitution of a methyl group $-CH_3$ in place of an atom of hydrogen in ethane will be more evident :

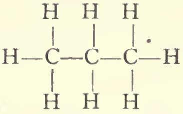


$$\mathrm{H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}H + Cl_2 \rightarrow H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}Cl + HCl}$$



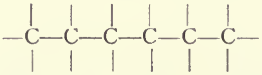
$$\begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{Cl}\\ \mathrm{Cl}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{H}\end{array} + 2\mathrm{Na} \rightarrow 2\mathrm{NaCl} + \begin{array}{c}\mathrm{H}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{H{-}C{-}H}\\ |\\ \mathrm{H}\end{array}$$

The formula of propane is more commonly written :



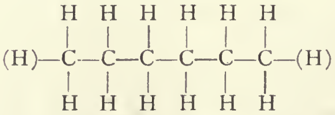
$$\mathrm{H{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}H}$$

The reason that so many hydrocarbons are known is that the carbon atoms may in this way be linked together forming a chain,



$$-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-$$

the valencies of the carbon atoms being satisfied by adding H to the vacant bonds. To each of these vacant bonds H atoms may be attached, thus :



$$\mathrm{(H){-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{-}(H)}$$

It is evident that the number of atoms of H is exactly double the number of atoms of carbon plus two atoms of hydrogen (H), at the ends of the chain.

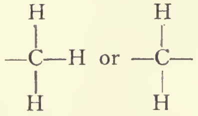
The formula of this series of hydrocarbons may therefore be written, C_nH_{2n+2}, termed the **generic formula** of the methane series.

From this formula, the molecular formula of any hydrocarbon of the series may be obtained, thus, if $n=16$, then $2n+2=34$, and formula = $C_{16}H_{34}$.

Other series of hydrocarbons will be dealt with later, but the generic formulae of a few may be now mentioned :

C_nH_{2n+2}............Methane series.
C_nH_{2n} ....Ethylene series.
C_nH_{2n-2}............Acetylene series.
C_nH_{2n-4}............Not important (only known incompletely).
C_nH_{2n-6}............Benzene series.

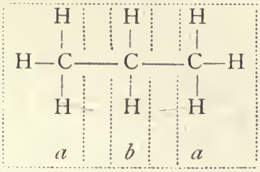
Prediction of number of hydrocarbons from formulae deduced by substitution. The formulae already dealt with for methane, ethane, and propane are commonly simplified to the ones shown below, though it should always be understood that the groups of elements : $—CH_3$ (methyl) or $—CH_2$ (methylene) represent symbolically :



$$\begin{array}{ccc} \text{H} & & \text{H} \\ | & & | \\ —\text{C}—\text{H} & \text{or} & —\text{C}— \\ | & & | \\ \text{H} & & \text{H} \end{array}$$

Methane............CH_4
Ethane ....$CH_3\cdot CH_3$ or $CH_3—CH_3$
Propane............$CH_3\cdot CH_2\cdot CH_3$ or $CH_3—CH_2—CH_3$

In deducing the formula of butane from propane by substitution of methyl $—CH_3$ in place of an atom of H, the substitution may be done in two ways, and this may be best explained by labelling the groups, in which the substitution is made, with small letters, *a*, *b*, *c*, etc.



......Propane,

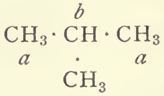
or

$$\underset{a}{CH_3}\cdot\underset{b}{CH_2}\cdot\underset{a}{CH_3}$$

The hydrogen atoms in each *a* group are all of equivalent value for substitution purposes, and whichever is replaced by the group methyl, $—CH_3$, the following formula is obtained :

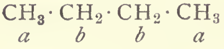
$$\underset{a}{CH_3}\cdot\underset{b}{CH_2}\cdot\underset{a}{CH_2}\cdot CH_3 \text{......Normal butane.}$$

By replacing one of the two atoms in the —CH_2— group or *b* group in propane, a second butane may be got thus :



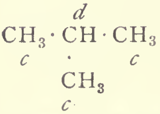
$$\mathrm{\underset{a}{CH_3}\cdot\underset{\substack{\cdot\\ CH_3}}{\overset{b}{CH}}\cdot\underset{a}{CH_3}}\ \text{......Isobutane.}$$

On this principle of substitution, these are the only possible butanes, and two only have been discovered. Similarly from the two butanes, the formulae of the three known pentanes may be deduced, and it should be noted that the theoretical deductions have always been found to agree with the number of compounds known, when these have all been discovered.



$$\mathrm{\underset{a}{CH_3}\cdot\underset{b}{CH_2}\cdot\underset{b}{CH_2}\cdot\underset{a}{CH_3}}$$

Normal butane. *a* groups are symmetrically disposed and also the *b* groups.



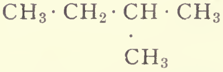
$$\mathrm{\underset{c}{CH_3}\cdot\underset{\substack{\cdot\\ CH_3\\ c}}{\overset{d}{CH}}\cdot\underset{c}{CH_3}}$$

Isobutane. *c* groups are symmetrically disposed.

Pentanes by substitution:

(*a*) $CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3$ Normal pentane.

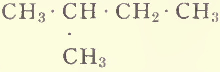
(*b*)



$$\mathrm{CH_3\cdot CH_2\cdot\underset{\substack{\cdot\\ CH_3}}{CH}\cdot CH_3}$$

Isopentane.

(*c*)

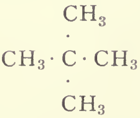


$$\mathrm{CH_3\cdot\underset{\substack{\cdot\\ CH_3}}{CH}\cdot CH_2\cdot CH_3}$$

Isopentane.

Inspection will show these to be identical in structure.

(*d*)



$$\mathrm{CH_3\cdot\underset{\substack{\cdot\\ CH_3}}{\overset{\substack{CH_3\\ \cdot}}{C}}\cdot CH_3}$$

Neopentane.

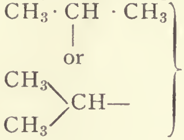
There are thus three pentanes, and three only have been discovered.

Methods of naming hydrocarbons.

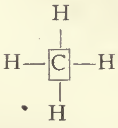
Straight and side chains. The normal compounds shown above will be noticed to have a straight chain of carbon atoms, and are termed **straight chain compounds.** The others have side groups introduced and are termed **side chain compounds.**

Normal, iso- and neo-hydrocarbons. In normal compounds, no carbon atom is attached to more than two substituting groups. In the iso-compounds, one C atom is attached to at least three substituting groups, and in the neo-compound, one C atom is attached to four groups. It may be noted here that a normal hydrocarbon has the highest B.P., and the neo-compound the lowest B.P.

Alkyl groups. From the hydrocarbons, certain groups of atoms, or radicals, may be obtained by the withdrawal of one atom of H in each case, and the monad radicals obtained in this way from the paraffin hydrocarbons are termed alkyl groups. The alkyl groups, which are in common use for naming compounds, are methyl, ethyl, normal propyl and isopropyl, and are derived from the hydrocarbons, thus :

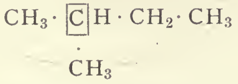
Hydrocarbons		
Name	Formula	Alkyl group
Methane	CH_4	$CH_3—$ Methyl.
Ethane	$CH_3 \cdot CH_3$	$CH_3 \cdot CH_2—$ or $C_2H_5—$ Ethyl.
Propane	$CH_3 \cdot CH_2 \cdot CH_3$	$CH_3 \cdot CH_2 \cdot CH_2—$ *n*-propyl.
		 $CH_3 \cdot \underset{\mid}{CH} \cdot CH_3$ or $(CH_3)_2CH—$ Isopropyl or *i*-propyl.

The more complex hydrocarbons are frequently named as **derivatives of methane,** in which the hydrogen atoms have been replaced by methyl, ethyl, etc. Isopentane and neopentane may be now named, and for this purpose it is necessary to decide upon the particular carbon atom which represents the C atom in the original methane molecule, or which may be called the methane nucleus. The most convenient one to take is represented $\boxed{C}$, though it should be understood that other C atoms might be accepted and alternative names given accordingly :



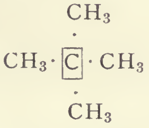
$$H—\underset{H}{\overset{H}{\boxed{C}}}—H$$

Methane



$$CH_3 \cdot \underset{CH_3}{\boxed{C}}H \cdot CH_2 \cdot CH_3$$

Isopentane or
dimethyl-ethyl-methane



$$CH_3 \cdot \underset{CH_3}{\overset{CH_3}{\boxed{C}}} \cdot CH_3$$

Neopentane or
tetramethyl-methane

In the isopentane, three H atoms have been withdrawn from the original methane molecule, and their places have been taken by two methyl ($—CH_3$) groups, and one ethyl ($CH_3 \cdot CH_2—$) group, so that the compound becomes dimethyl-ethyl-methane. Similarly in neopentane, the four hydrogen atoms in the original molecule of methane are replaced by four methyl groups, and it is named tetramethyl-methane.

In this method of naming, the groups introduced are given first (in any order), and the name of the compound (*e.g.*, methane) in which the substitution is made is given last.

Methane or marsh gas.

This compound is found in fire damp in coal mines, in the gas escaping from marshy pools, and is an important constituent (approximately 50 per cent.) of coal gas.

Preparation. It is prepared by heating anhydrous sodium acetate and an alkali (soda lime or barium hydroxide) together in a hard glass flask supported on its side.

$$CH_3.COONa+NaOH \rightarrow CH_4+Na_2CO_3$$

It may also be obtained by the reduction of methyl iodide in a methyl alcohol solution, the reducing agent being a zinc-copper couple, obtained by dipping zinc into a strong copper sulphate solution, which gives nascent hydrogen with the solvent.

$$CH_3I+2H \rightarrow CH_4+HI$$

Properties. Methane is a colourless gas, with a slight sweetish taste, practically odourless, lighter than air, almost insoluble in water and combustible, burning with an almost invisible flame.

$$\underset{\text{1 vol.}}{CH_4}+\underset{\text{2 vols.}}{2O_2} \rightarrow \underset{\text{1 vol.}}{CO_2}+2H_2O$$

It will thus be seen that for perfect combustion it requires 2 volumes of oxygen for each volume of methane, and with a less supply of oxygen than this, carbon monoxide or even H may be liberated. A mixture of 1 volume of CH_4 and 2 volumes of O is violently explosive, an experiment which may be safely done in a soda water bottle, wrapped in a towel before exploding the mixture.

With an excess of oxygen, or a supply sufficient for complete combustion, the equation above shows that methane always produces its own volume of carbon dioxide, and, as the volume of the latter is easily obtained by absorption with caustic potash solution, this method is used for getting the percentage of methane in a gaseous mixture in gas analysis.

Methane combines slowly with the halogens, particularly if exposed to sunlight.

Ethane.

Preparation. Ethane is prepared by methods similar to those for methane, *viz.*:

(1) By heating together sodium propionate and an alkali:

$$C_2H_5.COONa+NaOH \rightarrow C_2H_6+Na_2CO_3$$

(2) By the reduction of ethyl iodide:

$$C_2H_5I+2H \rightarrow C_2H_6+HI$$

(3) The hydrocarbons containing an even number of carbon atoms may be obtained by heating a halogen derivative with sodium, a method already referred to :

$$2CH_3I + 2Na \rightarrow 2NaI + C_2H_6$$

Properties. Ethane is a colourless gas, very slightly heavier than air, and burns with a flame somewhat more luminous than methane :

$$\begin{array}{llll} 2C_2H_6 + & 7O_2 \rightarrow & 4CO_2 + & 6H_2O \\ \text{2 vols.} & \text{7 vols.} & \text{4 vols.} & \end{array}$$

Higher hydrocarbons.

Normal pentane is a colourless liquid, B.P. 36° C.; it is used in the pentane lamp for producing a standard illuminant for photometric work.

Petroleum (American) is, as already mentioned, a complex mixture of paraffin hydrocarbons. These are not separated from the petroleum in a state of purity, but various liquids, which are mixtures of the paraffin hydrocarbons, are obtained from petroleum by fractional distillation. The following are some of the more important commercial products obtained :

A. **Light oils.**

Benzine	45°—60° C.
Gasoline	40°—70°.
Petroleum ether	70°—90°.
Benzoline	70°—95°.
Petrol	70°—120°.
Naphtha	95°—120°.
Ligroin (light petroleum)	120°—130°

B. **Burning oils.** Kerosene 180°—300° C.

C. **Lubricating oils.** Boiling at higher temperatures.
Vaseline used medicinally and as a lubricant.
Pitch. Used for cement, asphalt, varnishes and fuel.

Russian petroleum is somewhat similar in composition, but in addition contains other series of hydrocarbons. It yields, on distillation, products from which "benzine," kerosene, lubricating oils, etc., are obtained.

Paraffin wax, containing from $C_{23}H_{48}$ to $C_{29}H_{60}$ in the methane series, is obtained from East Indian petroleum, etc. ; its M.P. varies from 35° to 75° C.

Petrol is also obtained from petroleum as a special fraction, or mixture of liquids, containing some of the lower B.P. constituents.

The various products are valued by determinations of specific gravity, boiling point or the proportion distilling between certain temperature limits, flashing point in the case of burning and lubricating oils, the viscosity test in the case of lubricating oils, etc.

Lubricating oils. Determination of flashing point. The flashing point of an oil, mineral or lubricating, is the temperature at which sufficient inflammable vapour is evolved to fire or "flash" momentarily when a flame is applied. The test may be applied in an open crucible, *i.e.*, the **open test,** but more commonly, one of the forms of apparatus devised for the purpose is employed, in which the oil is heated in a closed vessel, which is momentarily opened during the application of a flame. For the application of this **closed test,** the "Abel" apparatus must be used for very low flashing substances, such as petroleum ether, acetone, etc., but for a petrol, or mineral, or lubricating oil, the Pensky-Martens apparatus is frequently used.

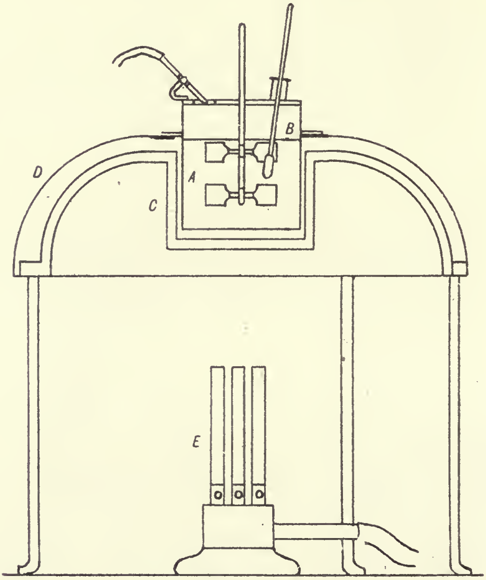


Fig. 89. Pensky-Martens apparatus for determining the flash point of an oil.

The Pensky-Martens apparatus. The oil-cup, *A* (Fig. 89), filled with oil to the mark, *B*, is surrounded by an air jacket, *C*, and a protective mantle, *D*, of brass lined with asbestos, the air jacket being heated by the triple burner, *E*. A suitable cover is provided with thermometer and stirrer, and with a revolving shutter turned by a milled head. Openings in the top are closed by the shutter, and a small jet flame is automatically plunged into the opening of the oil cup, *A*, when the shutter is moved.

The bath is heated till the temperature has risen to about 100° C., and the stirrer is then worked and the test is made, every 2° C., from about 120° C. and finally every 1° C., by depressing the small jet flame into the cup. The vapours may at first extinguish the jet flame, which may be re-lit at a small flame fed from a by-pass. The vapour inside the cup finally ignites and a flash is seen, and the temperature of the oil is then taken as the flashing point.

Fig. 90. The Gray flash point apparatus.

The experiment must not be repeated with the same specimen of oil, or a variable result will be obtained, due to the oil having lost some of its volatile constituents during the first test. A photograph of the Gray flash point apparatus, very similar to the above, is shown in Fig. 90.

The viscosity of an oil. The internal friction of the molecules in the case of a liquid is determined technically by measuring the viscosity, which is usually expressed relatively to a standard oil. Refined rape oil, with a sp. gr. 0·915 at 60° F., was the standard suggested by Sir Boverton Redwood for his viscometer, but for many purposes olive oil is now often taken as the standard.

Boverton Redwood's viscometer. In this instrument a measured quantity of oil is run out from an orifice under standard conditions, the standard rape oil under these conditions flowing at the rate of 50 c.c. in 535 seconds at 60° F.

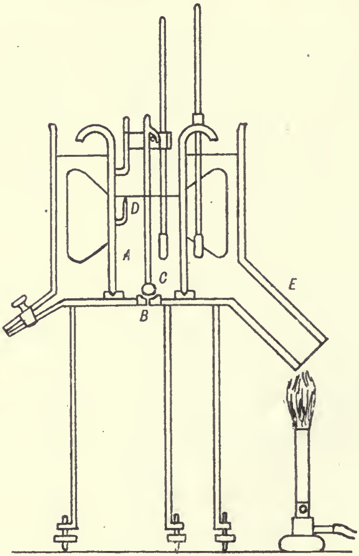


Fig. 91. Boverton Redwood viscometer for determining the viscosity of an oil.

The oil cylinder, *A* (Figs. 91 and 92), is of silvered brass, about 2″ diameter and $3\frac{1}{2}$″ deep, and is furnished with an agate jet, *B*, closed by a silvered-brass plug, *C*. The cylinder is filled with oil up to the point of a bracket, *D*, and the temperature of the oil is taken with a thermometer. The cylinder is surrounded by a water jacket heated to a definite temperature by applying heat to the side tube, *E*, and the water is stirred by a suitable stirrer on which is mounted a thermometer for taking the temperature of the water bath, or if temperatures above 95° C. are to be used then mineral oil is employed in the outer bath. The oil heated to the same temperature as the outer bath is poured into the cylinder to the required height, and the time in seconds is taken for 50 c.c. of the oil to flow out into a graduated flask.

Care must be taken that the level of the oil is exactly on the point of the bracket at the commencement, and that the temperature of the oil is constant during the time of the experiment. The viscosity of the oil in practice is compared with refined rape oil = 100.

The sp. gr. of the rape oil at 60° F. is 0·915, and if the sp. gr. of the oil is different from this, then the viscosity is obtained, thus:

$$V \text{ (viscosity)} = \frac{n \times 100 \times s}{535 \times \cdot 915},$$

where n = time in seconds for 50 c.c. of oil to flow out,
s = sp. gr. of oil.

The following are, approximately, some of the constants of oils in common use.

Name of oil	Specific gravity at 60° F.		Flashing point
	American	Russian	
Spindle oils for spinning machinery	·840–·907	·800–·830	160°–200° C.
Lubricating oils for light machines, shafting, light motors, etc.	·875–·914	·900–·915	170°–220° C.
Cylinder oils	·883–·895	·909–·932 or even up to ·950	220°–315° C.

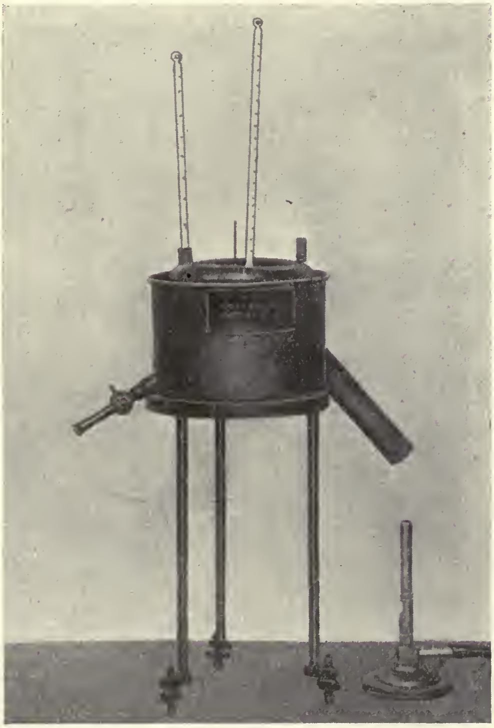


Fig. 92. The Boverton Redwood viscometer.

The following are a few viscosities taken by means of the Boverton Redwood viscometer at 60° F.:

Name of oil	Sp. gr. at 60° F.	Secs., flow of 50 c.c. at 60° F.	Viscosity
Refined rape oil	·915	540	100
Sperm oil	·880	177	32
Neat's foot oil	·916	470	87
American mineral oil	·885	105	19
" "	·913	295·5	54
" "	·923	680	127
Russian mineral oil	·909	1235	227
" "	·915	1980	366

The following times of flow in seconds for 50 c.c. of oil from Boverton Redwood's viscometer have been obtained with the following standard oils:

	Name of oil	Temperature	
		70° F.	100° F.
Used for spindles in textile work	Pale, sp. gr. ·865	64	48
	" " ·875	110	65
	" " ·885	172	87
	" " ·900–·907	315	138
	XXX spindle	344	150
	Queen's spindle	337	136
	H.V. pale oil	479	185
	Rose oil	330	124
Engine oils	Red engine oil	637	240
	Special red engine oil	890	285
	Bayonne engine oil	701	263
	Solar red engine oil	585	225
	Olive oil	—	185
	Arctic sperm oil	182	101
	Southern sperm oil	159	89

	Name of oil	Temperature		
		200° F.	300° F.	400° F.
Cylinder oils	A cylinder	128	—	37
	N cylinder	139	47	40
	Cosmos	123	—	36
	Loco cylinder	234	50	42

In the case of textile machinery, ring spindles, running at high velocities such as 10,000 revolutions per minute, are commonly lubricated by mineral oils having a low viscosity about equal to that of sperm oil at 60° F. For mule spindles, an oil having a viscosity about 2 or 3 times that of sperm oil at 60° F. is employed, and, although a pure mineral oil is often used, a mixture of mineral oil and 10 per cent. to 20 per cent. of sperm oil is more commonly employed.

For looms, a mineral oil is employed with a viscosity approximately 1·5 times the viscosity of olive oil. Mineral oils stain cotton and woollen goods, and, as it is difficult to remove the stains entirely, fixed oils, such as sperm, olive, etc., or mixtures containing a high percentage of fixed oils are commonly used when the fabric is liable to be splashed by the lubricant.

There has recently been put on the market by Dr L. L. Lloyd a treated mineral oil, **pullwulol**, principally for the oiling of wool, which is unoxidisable, and consequently does not stain the material; further, it is easily removed by washing.

Mineral oil with a viscosity from two-thirds to approximately three times the viscosity of rape oil at 60° F. is used for motors and dynamos, according to the power, speed, etc., of the machine.

CHAPTER XXIII

HALOGEN DERIVATIVES OF THE HYDROCARBONS

METHYL CHLORIDE: CHLOROFORM: CARBON TETRACHLORIDE: CHLOR-DERIVATIVES OF ETHANE: DETERGENTS IN TEXTILE OPERATIONS.

Halogen substitution products.

Halogen derivatives may be obtained from methane, by substitution, by gradually replacing the hydrogen by chlorine, bromine, or iodine, thus:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$
$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$
$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$
$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

A similar series of bromine and iodine derivatives may be obtained, and a similar process of substitution may be employed to obtain derivatives from ethane and the higher hydrocarbons. Some of these halogen derivatives have been or are used in certain textile operations as solvents, but the importance of these bodies lies more in the fact that they are, in many cases, used so largely in organic preparations or manufacturing processes. Only the more important of the compounds will be dealt with.

Methyl chloride, CH_3Cl. This is obtained (1) by the action of chlorine upon methane, (2) by the action of hydrochloric acid gas on methyl alcohol, preferably in the presence of a small quantity of zinc chloride to prevent the reversal of the reaction:

$$\underset{\text{methyl alcohol}}{CH_3OH} + HCl \rightarrow CH_3Cl + H_2O$$

It is manufactured by other processes, and is used in the preparation of dyestuffs.

It is a colourless gas, soluble in water, and burning with a greenish flame; it is easily liquefied, the liquid boiling at – 24° C.

Methylene dichloride, CH_2Cl_2, is a colourless liquid, boiling at 41° C., and is obtained by the reduction of chloroform.

Chloroform (trichlor-methane), $CHCl_3$. Chloroform is prepared by mixing 200 grams of bleaching powder with 750 c.c. of water to a cream, and distilling in a 2-litre flask with 50 c.c. of alcohol on a water bath. The heating at first is gradual, and a long condenser must be used to condense the chloroform, the heating being continued as long as chloroform distils over. The following actions take place:

$$\underset{\text{alcohol}}{CH_3\cdot CH_2OH} + Cl_2 \rightarrow \underset{\text{aldehyde}}{CH_3\cdot CHO} + 2HCl$$

$$CH_3\cdot CHO + 3Cl_2 \rightarrow \underset{\substack{\text{trichlor-aldehyde}\\ \text{or ``chloral''}}}{CCl_3\cdot CHO} + 3HCl$$

The chloral is decomposed by the alkali, $Ca(OH)_2$, in the bleaching powder forming chloroform and calcium formate.

$$2CCl_3\cdot CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + \underset{\text{calcium formate}}{(H\cdot COO)_2Ca}$$

The liquid distilling over is a mixture of chloroform and water, the latter collecting as a lighter layer and containing some chlorine in solution. The layers are separated by means of a separating funnel, the oily liquid shaken with a caustic soda solution to remove traces of chlorine, and after standing for about 5 minutes the lower oily liquid is removed. The chloroform is again washed, in a similar manner, twice with water, and dried by putting a little granular anhydrous calcium chloride into the liquid. It is finally redistilled and its boiling point taken.

Properties. A colourless liquid, B.P. 62° C., sp. gr. 1·5. It is extensively used as a solvent, and as an anaesthetic.

Carbon tetrachloride, CCl_4, is prepared (1) by the action of chlorine on boiling chloroform, (2) by the action of chlorine on a mixture of carbon disulphide and a small quantity of antimony pentachloride.

$$CS_2 + 3SbCl_5 \rightarrow CCl_4 + 3SbCl_3 + S_2Cl_2$$
$$SbCl_3 + Cl_2 \rightarrow SbCl_5$$

The liquid is distilled, the distillate shaken with potash to remove disulphur dichloride, S_2Cl_2, and finally redistilled.

Properties. It is a heavy liquid, B.P. 77° C., sp. gr. 1·6, and non-inflammable.

Carbon tetrachloride is not soluble in water, nor in alcohol up to 75 per cent. strength, but is soluble in a great many other reagents, *e.g.*, chloroform, acetic ether, petroleum and its distillates, etc. Being non-inflammable and non-explosive, but acting as a good solvent for oils, fats, waxes, etc., it is largely used as a detergent, especially as it does not affect the colours of dyed textile fabrics. It is put on the market under various trade names, **anti-flammin**, etc., and is also used in the manufacture of **tetrapol**.

Methyl and ethyl iodides, CH_3I and C_2H_5I, are largely used in organic preparations, but the actual preparation of these bodies themselves is hardly of importance to the textile student.

Chlorine derivatives of ethane. Ethane forms halogen derivatives, which are similar to those obtained from methane in many respects, thus ethyl chloride is produced similarly to methyl chloride.

Some of the chlor derivatives of ethane are of importance as industrial solvents, since they are non-inflammable and non-explosive, so that they may be used with absolute safety, whilst they may be obtained with a wider range in boiling points. The solvent character is extremely high, and they are being employed in detergents of the "tetrapol" class, these latter bodies being good solvents for grease, fats, etc., and being miscible with water and producing emulsions they are useful for cleansing and scouring woollen yarns and other materials.

The following are of commercial importance :

Symmetrical tetrachloro-ethane, $CHCl_2 \cdot CHCl_2$, B.P. 147° C., sp. gr. 1·6, is not very volatile and is slightly anaesthetic. It is slightly soluble in water, dissolves sulphur on heating, attacks iron and copper if moisture is present, and is decomposed appreciably by strong alkalis. It is suitable for high temperature extractions, particularly for extracting sulphur. It is a good solvent for resins, fats and oils, and is likely to find considerable application in the paint and varnish industry. It is a good solvent for cellulose acetate, and is stated to be the cheapest solvent yet suggested for this substance in the production of cinematograph films. It also finds useful applications in **waterproofing, particularly in aeroplane fabrics** (see Chapter XXXVIII, p. 341).

Pentachloro-ethane, $CHCl_2 \cdot CCl_3$, B.P. 159° C., sp. gr. 1·7, is similar in its applications to the tetrachlor compound and is particularly suitable as a solvent for cellulose acetate.

Hexachloro-ethane, C_2Cl_6, is a solid substance.

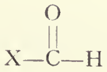
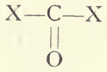
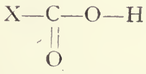
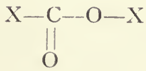
CHAPTER XXIV

THE ALCOHOLS AND ETHERS

OXYGEN DERIVATIVES OF HYDROCARBONS: METHYL AND ETHYL ALCOHOLS: ENZYMES: FERMENTATION: INDUSTRIAL SPIRIT: GLYCEROL: ETHER: EXTRACTION OF GREASE FROM TEXTILE MATERIALS.

Oxygen derivatives of hydrocarbons.

The principal series of oxygen derivatives are summarised below, the compounds derived from and corresponding to methane and ethane being given, and in the last column of the table the characteristic group of atoms and its structure is given for each series.

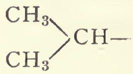
Hydrocarbons	CH_4 methane	$CH_3 \cdot CH_3$ ethane	**Characteristic Group**
Mono-halogen derivatives	CH_3Cl methyl chloride	$CH_3 \cdot CH_2 \cdot Cl$ ethyl chloride	**X = alkyl group**
Alcohols	$CH_3 \cdot OH$ methyl alcohol	$CH_3 \cdot CH_2 \cdot OH$ ethyl alcohol	X—OH
Ethers	$CH_3 \cdot O \cdot CH_3$ methyl ether	$C_2H_5 \cdot O \cdot C_2H_5$ ethyl ether	X—O—X
Aldehydes	$H \cdot CHO$ formaldehyde	$CH_3 \cdot CHO$ acetaldehyde	 $\mathrm{X{-}\overset{O}{\overset{\|}{C}}{-}H}$
Ketones	—	$CH_3 \cdot CO \cdot CH_3$ acetone	 $\mathrm{X{-}\underset{O}{\underset{\|}{C}}{-}X}$
Acids	$H \cdot COOH$ formic acid	$CH_3 \cdot COOH$ acetic acid	 $\mathrm{X{-}\underset{O}{\underset{\|}{C}}{-}O{-}H}$
Ethereal salts or esters	$H \cdot COOCH_3$ methyl formate	$CH_3 \cdot COOC_2H_5$ ethyl acetate	 $\mathrm{X{-}\underset{O}{\underset{\|}{C}}{-}O{-}X}$

Primary, secondary and tertiary radicals. The alkyl groups derived from hydrocarbons by the withdrawal of an atom of hydrogen are classed as primary, secondary, and tertiary radicals, and this method is used for naming the compound and indicating its constitution. This is of importance in the alcohols, as these different groups confer particular properties on the alcohols.

A primary radical is one in which the atom of carbon with the vacant bond is attached directly to one substituting group only, thus:

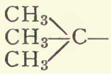
CH_3—methyl, $CH_3 \cdot CH_2 \cdot CH_2$—primary propyl.

A secondary radical is one in which the atom of carbon with the vacant bond is attached directly to two substituting groups, thus:



secondary propyl.

A tertiary radical is one in which the atom of carbon with the vacant bond is attached directly to three substituting groups, thus:



tertiary butyl.

Relationship between alcohols, aldehydes, ethers, and ketones. As seen from the above table, the compounds known as alcohols are derived from hydrocarbons, or mono-halogen derivatives of hydrocarbons, by replacement of hydrogen or an atom of the halogen by the hydroxyl group (—OH).

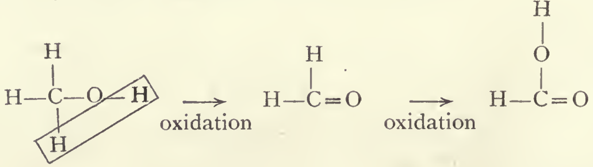
The aldehydes are oxidation products of the primary alcohols, and are formed from them by the removal of two atoms of hydrogen from the alcohol molecule, thus:

$$CH_3 \cdot OH + O \rightarrow H \cdot CHO + H_2O$$

The acids are further oxidation products of the aldehydes, thus:

$$H \cdot CHO + O \rightarrow H \cdot COOH$$

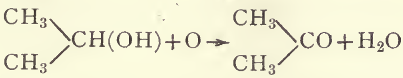
We can therefore pass from a primary alcohol to an aldehyde, and then to an acid by suitable processes of oxidation, thus:



The alcohols correspond to the compounds known as hydroxides (or alkalis) amongst the inorganic compounds, and in some respects in their combination with acids are similar in properties. The ethers similarly may be looked upon as oxides, and correspond to the bases in inorganic chemistry; in both sets of compounds, the alkyl groups take the place of atoms of metals in alkalis and bases. This relationship may be summarised thus:

$$\text{K—OH alkali} \longrightarrow CH_3\cdot OH \text{ alcohol}$$
$$\text{K—O—K base} \longrightarrow CH_3\cdot O\cdot CH_3 \text{ ether}$$

The ketones are oxidation products of secondary alcohols, thus isopropyl alcohol, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!CH(OH)$, or secondary propyl alcohol yields acetone:



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!CH(OH) + O \rightarrow \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!>\!CO + H_2O$$

The secondary alcohol group is $>CH(OH)$, and this is converted into the ketonic group $>CO$ by oxidation.

The ketones bear the same relationship to the aldehydes, that the ethers bear to the alcohols, as shown by the following formulae:

$CH_3—O—\boxed{H}$ alcohol	$\xrightarrow{\hspace{2cm}}$ H replaced by $—CH_3$	$CH_3—O—CH_3$ ether
$CH_3\cdot C\boxed{H}O$ aldehyde	$\xrightarrow{\hspace{2cm}}$ H replaced by $—CH_3$	$CH_3\cdot CO\cdot CH_3$ ketone

The tertiary alcohols yield neither aldehydes nor ketones, but are broken up by oxidation.

Alcohols.

General method of preparing alcohols. Alcohols are obtained by the action of silver hydroxide on a halogen derivative of a hydrocarbon, thus:

$$C_2H_5I + AgOH \rightarrow C_2H_5OH + AgI$$

Methyl alcohol, CH_3OH, is contained in the acid liquid, known as pyroligneous acid, which is obtained in the destructive distillation of wood. In addition, the spirit contains acetic acid, acetone and water. The pyroligneous acid is first fractionated, and quicklime added to remove water and acetic acid, which thus combine with the CaO forming $Ca(OH)_2$ and $(CH_3\cdot COO)_2Ca$.

The residual liquid forms wood spirit or commercial methyl alcohol, but still retains acetone, though in the manufacture of varnishes, etc., the presence of the acetone improves its solvent properties. The alcohol is further purified by forming a crystalline compound with $CaCl_2$, having the formula, $CaCl_2$, $4CH_3OH$. After drying, the crystallised compound may be decomposed by distilling with water, and the aqueous distillate is again dehydrated by means of quicklime.

Properties. Colourless liquid, B.P. 67° C., sp. gr. 0·796 at 20° C. In the pure state it is poisonous and in small quantities intoxicates. It is a good solvent for fats, resins, etc., and is used in the manufacture of varnishes, methylated spirit, and dyestuffs.

The chemical properties, which are general reactions for the alcohols, are:

(1) Sodium acts upon it forming a compound, sodium methylate, belonging to the class known as alcoholates.

$$2CH_3OH + 2Na \rightarrow 2CH_3 \cdot ONa + H_2$$

(2) When oxidised it forms an aldehyde (formaldehyde) and then an acid (formic acid).

(3) When acted upon by PCl_5, the alcoholic —OH group is replaced by Cl.

$$CH_3OH + PCl_5 \rightarrow CH_3Cl + POCl_3 + HCl$$

(4) With an acid it acts in a similar manner to an alkali forming a salt, thus:

$$CH_3OH + H_2SO_4 \rightarrow CH_3HSO_4 + H_2O$$

The student should compare this reaction with that of KOH on H_2SO_4 forming $KHSO_4$.

Ethyl alcohol, $CH_3 \cdot CH_2OH$ or C_2H_5OH (spirits of wine). Ethyl alcohol, or the substance commonly known as alcohol, may be obtained by the general reaction described above, but is prepared commercially by a process known as **fermentation.**

In this action yeast is added to a solution of certain sugars, of which grape sugar, or glucose ($C_6H_{12}O_6$), may be considered to be a typical member, the yeast breaking up the sugar molecule into alcohol and carbon dioxide, thus:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

The **yeast** is a form of vegetable life, and, during the process of fermentation, the yeast plant undergoes the process of reproduction, and the new cells, which are formed, can set up the process of fermentation.

In quite recent times, the views regarding fermentation have undergone considerable modifications, and Buchner has shown that the process is due to the action of a body named "**zymase.**" He has extracted this substance by pressure from the yeast cells, and the liquid containing the zymase, which is quite free from any form of life, will bring about the process of fermentation.

Enzymes. Zymase belongs to a class of bodies now termed enzymes, and Buchner classifies these into three main groups:

(1) **Dissociating enzymes,** such as yeast, which bring about the decomposition of certain sugars.

(2) **Hydrolytic enzymes**, such as diastase, present in germinating grain, or malt, which decompose certain bodies by the action of water producing fermentable sugars. Cane sugar, $C_{12}H_{22}O_{11}$, and starch, $(C_6H_{10}O_5)_n$, may be hydrolysed in this way, thus:

$$\underset{}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

$$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6$$

This action may be slowly brought about by yeast, owing to the presence of a hydrolytic enzyme, **invertase**, which attacks the cane sugar, so that the latter may be slowly fermented by means of yeast. The hydrolytic action may also be brought about by heating the cane sugar or starch solution with a small quantity of mineral acid.

(3) **Oxidising enzymes**, such as **mycoderma aceti**, which bring about the oxidation of ordinary alcohol with the production of acetic acid.

Manufacture of alcohol. Potatoes, grain, etc., containing starch are first digested at about 140° F., with water and the liquid mash is pressed out. The mash is further treated at 140° F. with malt, the diastase present in the malt converting the starch into fermentable sugar. The liquid, known as wort, is then cooled to about 60° F., yeast added and fermented. After fermentation, the liquid is fractionally distilled, and the crude spirit is filtered through charcoal, after which it is again subjected to fractional distillation.

Three fractions are collected (1) a volatile portion containing aldehydes; (2) alcohol or spirit; (3) higher alcohols, known commonly as **fusel oil**.

The spirit fraction is mixed with quicklime, redistilled, and put on the market as **absolute alcohol**. It still contains about 0·5 per cent. of water, which is most difficult to remove, but may be got rid of by the action of a small quantity of sodium and redistilling.

Alcoholic beverages are prepared by similar processes.

Properties. Alcohol is a colourless liquid, with a pleasant odour, B.P. 78° C., solidifying point −130° C. When pure it is poisonous, but in small quantities intoxicates. It is miscible with water in all proportions, and is an excellent solvent in the production of varnishes, etc. It burns with a bluish flame. The chemical reactions are similar to those of methyl alcohol, reacting with sodium, phosphorus pentachloride, acids, and it is oxidised with the formation of acetaldehyde and acetic acid.

Methylated spirit contains 90 per cent. of crude alcohol, 10 per cent. crude wood spirit, and small quantities of light petroleum. The latter makes it unfit for consumption as a beverage, but is objectionable for chemical processes where the liquid has to be mixed with water, owing to the milkiness which is produced.

Industrial spirit is now sold, however, for trade purposes under certain restrictions, and this spirit, containing 90 per cent. alcohol, may be mixed in any proportion with water.

Poly-hydric alcohols—glycerol. The two common alcohols, already described, are examples of mono-hydric alcohols, containing only one alcoholic hydroxyl group in the molecule, but alcohols may also be obtained containing two or more hydroxyl groups, thus:

$$\begin{array}{ccc} CH_3\cdot CH_3 & CH_3\cdot CH_2\cdot OH & CH_2(OH)\cdot CH_2\cdot(OH) \\ \text{ethane} & \text{alcohol} & \text{glycol} \\ & \text{(mono-hydric)} & \text{(di-hydric)} \end{array}$$

$$\begin{array}{cc} CH_3\cdot CH_2\cdot CH_3 & CH_2(OH)\cdot CH(OH)\cdot CH_2(OH) \\ \text{propane} & \text{glycerol or glycerine} \\ & \text{(tri-hydric)} \end{array}$$

Glycerol is found in nature in fats and oils in combination with organic acids, and will be dealt with more in detail later in considering these substances.

Ethers.

The ethers, as already shown, are oxides of alkyl radicals, and the two radicals in the molecule may either be the same or different in character, thus giving rise to the following:

(1) **simple ethers**, such as $C_2H_5—O—C_2H_5$, ethyl ether, or

(2) **mixed ethers**, such as $CH_3—O—C_2H_5$, methyl ethyl ether.

General methods of preparation. (1) An alcoholate is acted upon by a halogen derivative of a hydrocarbon, *e.g.*, sodium ethylate and ethyl iodide react thus:

$$C_2H_5ONa + C_2H_5I \rightarrow NaI + C_2H_5—O—C_2H_5$$

(2) An alkyl derivative of sulphuric acid is acted upon by an alcohol, *e.g.*, ethyl sulphuric acid and ethyl alcohol react thus:

$$C_2H_5OH + H_2SO_4 \rightarrow \underset{\text{ethyl sulphuric acid}}{C_2H_5HSO_4} + H_2O$$

$$C_2H_5HSO_4 + C_2H_5OH \rightarrow \underset{\text{ether}}{C_2H_5—O—C_2H_5} + H_2SO_4$$

Preparation of ether (ethyl oxide or **sulphuric ether**). A mixture of equal volumes of ethyl alcohol and concentrated sulphuric acid is made and heated in a distilling flask to 140° C. in an oil bath as shown in Fig. 93. Ordinary alcohol is dropped near to the surface of the liquid at the rate at which the ether distils over, and a mixture of water, alcohol and ether is obtained in the receiver. A long condenser, at least 24″ long in the body, should be used, otherwise it is impossible to condense all the ether, and the receiver should be a filter flask connected tightly to the condenser, the side tube being provided with a rubber tube to lead away any ether vapour to a point near the floor.

The distillate is washed with (*a*) caustic soda solution to remove SO_2, (*b*) a strong brine solution to remove alcohol, (*c*) water to remove brine, and is then dried by granular calcium chloride and redistilled, its boiling point being taken.

Properties. Ether is a colourless, very mobile liquid, with a pleasant odour. Its boiling point is 35° C., and the vapour is very heavy and inflammable. It forms a highly explosive mixture with air or oxygen, the following action taking place:

$$\underset{\text{1 vol. ether vapour}}{(C_2H_5)_2O} + \underset{\substack{\text{6 vols. O} \\ \text{or 30 vols. air}}}{6O_2} \rightarrow 4CO_2 + 5H_2O$$

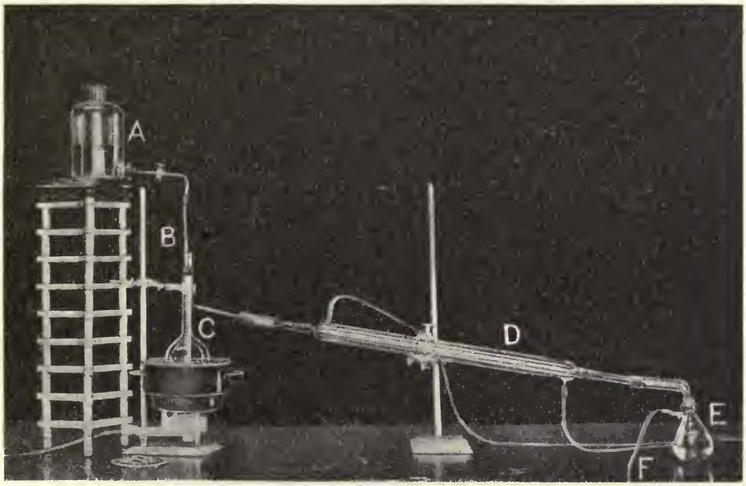


Fig. 93. Preparation of ether. *A*, store bottle containing alcohol; *B*, dropping tube; *C*, distilling flask; *D*, condenser; *E*, collecting flask; *F*, tube to lead vapour to floor level.

Great care should therefore be taken in the use of ether, as owing to the low boiling point it has a high vapour pressure at ordinary temperatures, and the atmosphere in a bottle partly filled with ether is inflammable. In pouring ether out of a bottle, the ether vapour may roll on a bench for considerable distances and ignite at a distant flame, the flame running back to the source of the vapour. If the vapour ignites at the mouth of a bottle of ether, the stopper should be at once inserted, or the palm of the hand put on the bottle to cut off the air.

The tendency of the vapour to roll and ignite may be shown by pouring ether vapour, from a small quantity of liquid ether in a porcelain dish, down an inclined V-shaped trough of cardboard or metal, with a flame at the lower end. The flame will pass back and ignite the ether in the dish; the flame in the dish may be extinguished by a duster.

Ether produces a great degree of cold on evaporation, and a block of wood may be frozen to a wet flask containing ether, by blowing a current of air vigorously through the liquid ether.

Extraction of fats, oils or grease from textile materials. Ether is an excellent solvent for fats, oils, resins, greases, etc., and is frequently used for this purpose for extracting oils or grease from textile materials.

The apparatus shown in Fig. 94 is used for extracting grease from wool, yarns, etc., for the purpose of estimating the percentage of fatty matter in the textile material.

A weighed quantity of the material is put into the Soxhlet extractor, *A*, and ether is heated in the weighed flask, *B*, by a hot water bath until the ether boils vigorously. The ether vapour passes up the wide tube, *C*, into the reflux condenser, *D*, where the ether is condensed, the liquid ether dripping on to the material in *A*. The extraction of the grease begins, and when the solvent has accumulated to the level of the upper bend of the siphon tube, *E*, the liquid ether, with dissolved fat, is automatically siphoned over to the flask, *B*.

The process is repeated as many times as may be necessary to extract the whole of the grease, from 6 to 10 extractions being usually sufficient, the material being each time treated with fat-free ether.

The ether is finally distilled off from the flask by connecting a bent tube and condenser, thus collecting the ether for further use, and the fat or grease remaining in the flask is dried by heating it in a steam oven for a short time. The flask is finally weighed, the increase in weight giving the weight of fat in the weighed quantity of material, and the percentage may be calculated.

Solution of ether in water. Ether is slightly soluble in water and water is slightly soluble in ether. This may be shown by shaking water and ether together in a stoppered cylinder. Care must be taken to hold the stoppers tightly, to prevent the pressure of the vapour blowing them out, and the tap may be turned with the cylinder inverted, after shaking, to release the pressure of the vapour.

The liquid is allowed to stand for 5 or 10 minutes, so that the layers may be separated, the layers consisting of saturated solutions of water in ether, and ether in water. If a little of the lower water layer is run off and heated in a test tube, the ether vapour evolved may be burnt at the mouth of the tube. The addition of anhydrous copper sulphate to the ether layer may be used to show the presence of water. The ether layer is best dried with granular calcium chloride.

In some cases it is necessary to wash an ethereal solution containing fat or grease with water, and if the experiment is a quantitative one the amount of water should be kept to a minimum, otherwise a serious loss of ether with dissolved fat may result. In such a case it is advisable to use 2 or 3 portions of water, using only a very small quantity each time, so as to reduce the loss to a negligible quantity.

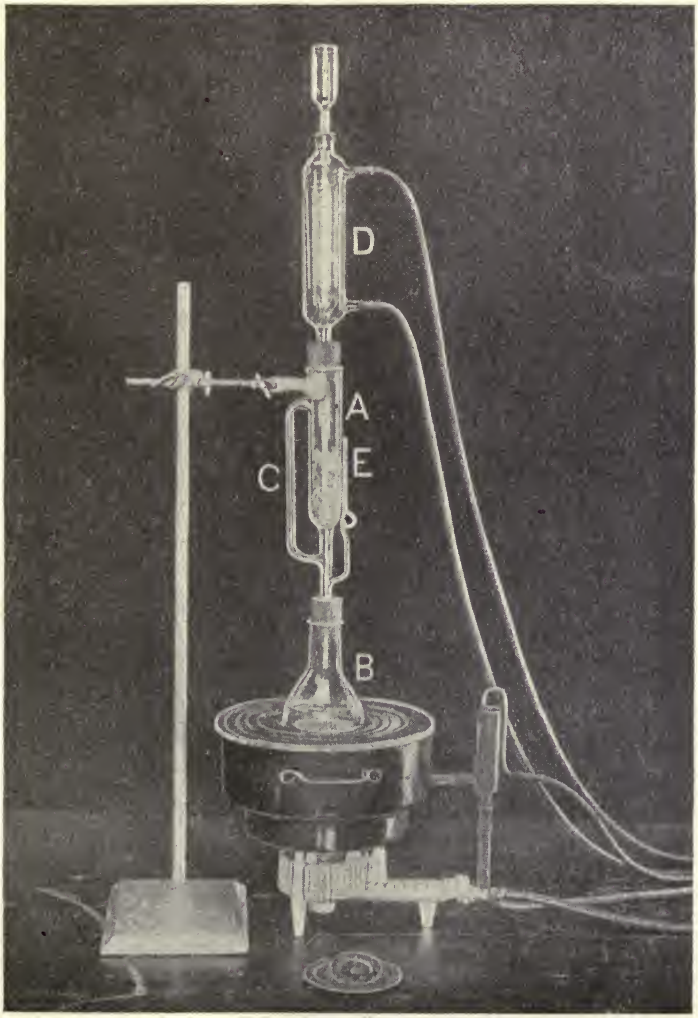


Fig. 94. Extraction of grease from yarn. Used in estimating the grease or oil in wool, yarn, etc.

CHAPTER XXV

ALDEHYDES AND KETONES

FORMALDEHYDE OR "FORMALIN": ACETALDEHYDE: FORMALDEHYDE HYDROSULPHITES: USE OF THESE AS DISCHARGING AGENTS IN TEXTILE OPERATIONS: ACETONE.

Aldehydes and ketones.

The term aldehyde signifies alcohol without hydrogen and indicates the mode of formation, these compounds being obtained by the withdrawal of two atoms of H by means of suitable oxidising agents from primary alcohols, one hydrogen being taken from the hydroxyl (OH) group, and the second from the adjacent substituting group.

As the primary alcohol group is $—CH_2OH$, this is converted by oxidation into the aldehyde group, $—CHO$, thus:

$$\underset{\text{ethyl alcohol}}{CH_3\cdot CH_2OH} + O \rightarrow \underset{\text{acetaldehyde}}{CH_3\cdot CHO} + H_2O$$

The aldehydes are named from acids which they produce on further oxidation.

In a similar manner, secondary alcohols contain the secondary alcoholic group, $=CH(OH)$ and by oxidation this group is converted into the ketonic group, $=CO$, thus giving rise to the compounds known as ketones, thus:

$$\underset{\text{secondary propyl alcohol}}{(CH_3)_2 : CH(OH)} + O \rightarrow \underset{\text{acetone}}{(CH_3)_2 : CO} + H_2O$$

Formaldehyde. Preparation. This compound is prepared by oxidation of methyl alcohol, the latter being drawn as a gas mixed with air over a heated copper or platinum spiral. The action is best carried out by passing a current of air through warm methyl alcohol, and then passing the mixed gases through a heated glass tube containing the metal. The formaldehyde gas is absorbed in water forming a solution.

Properties. At ordinary temperatures formaldehyde is a gas, but may be liquefied at $-21°$ C. It is sold in the form of a 40 per cent. solution in water known as **formalin.** The compound readily changes in the presence of a trace of strong sulphuric acid to a solid crystalline compound, in which several molecules, possibly three, of formaldehyde combine together, the formula being represented $(CH_2O)_x$, as the value of x has not been determined with certainty.

This property of forming a more complex body of the same percentage composition, by the union of two or more molecules, is termed **polymerisation**, and the compound $(CH_2O)_x$, **para-formaldehyde**, is said to be a polymer of formaldehyde. The para-formaldehyde again forms formaldehyde when volatilised.

Formaldehyde is an important disinfectant and antiseptic, and it also possesses the property, when added in small quantities to gelatine, of rendering the gelatine insoluble in water. It has been used in the artificial silk industry for this purpose, and also for waterproofing.

The other properties of formaldehyde will be dealt with under general reactions of aldehydes.

Acetaldehyde, $CH_3 \cdot CHO$. Preparation. This compound is prepared by oxidising ethyl alcohol by means of a mixture of sodium dichromate and sulphuric acid. The reaction is best carried out by running from a tap funnel a mixture of 200 parts by weight of sodium dichromate, 200 parts of water and 100 parts of alcohol into 100 parts of concentrated sulphuric acid and 200 parts by weight of water. The mixture is distilled, and the distillate condensed by means of an ordinary condenser and a receiving flask surrounded by ice and salt. The following reaction takes place:

$$3C_2H_5OH + Na_2Cr_2O_7 + 4H_2SO_4 \\ \rightarrow Na_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3CH_3 \cdot CHO$$

The distillate contains a mixture of acetaldehyde, alcohol and water, and is redistilled in a flask attached to a reflux condenser, as shown in Fig. 95, the alcohol and water being condensed and flowing back into the flask, whilst the aldehyde passes over and is absorbed in ether in the two bottles immersed in water.

Ammonia gas is then passed into the ethereal solution, thus forming acetaldehyde ammonia, a solid compound which crystallises as the ether evaporates. By distilling the aldehyde ammonia with dilute sulphuric acid, acetaldehyde may be liberated and condensed by means of ice and salt. It is dehydrated by means of granular calcium chloride.

Properties. It is a colourless volatile liquid, with a choking odour, boiling at 21° C. It is readily polymerised on the addition of a trace of sulphuric acid forming a colourless liquid, boiling at 124° C., named **paraldehyde** $(CH_3 \cdot CHO)_3$. This is reconverted into acetaldehyde by distilling with dilute sulphuric acid. Acetaldehyde possesses all the characteristic properties of aldehydes.

Characteristic properties of aldehydes. (1) They are all good reducing agents, reducing silver and cupric salts to metallic silver or cuprous compounds, the aldehyde at the same time being oxidised to an acid.

Silver nitrate in an ammoniacal solution may be readily reduced in this way giving metallic silver, a reaction often used for **silvering glass.**

The action may be shown by well cleaning a test tube with (1) hot nitric acid, (2) hot strong KOH solution and washing well with water after each treatment. The action is more successful if a little stannous chloride solution is run over the surface of the cleansed glass, and then again washing once or twice with water. The silver nitrate solution, made slightly alkaline with ammonia, is poured into the tube and a drop or two of acetaldehyde or formalin added. On gently heating, a bright deposit of silver forms on the glass surface. The success of the experiment depends entirely on the cleanliness of the glass, and particularly its freedom from grease.

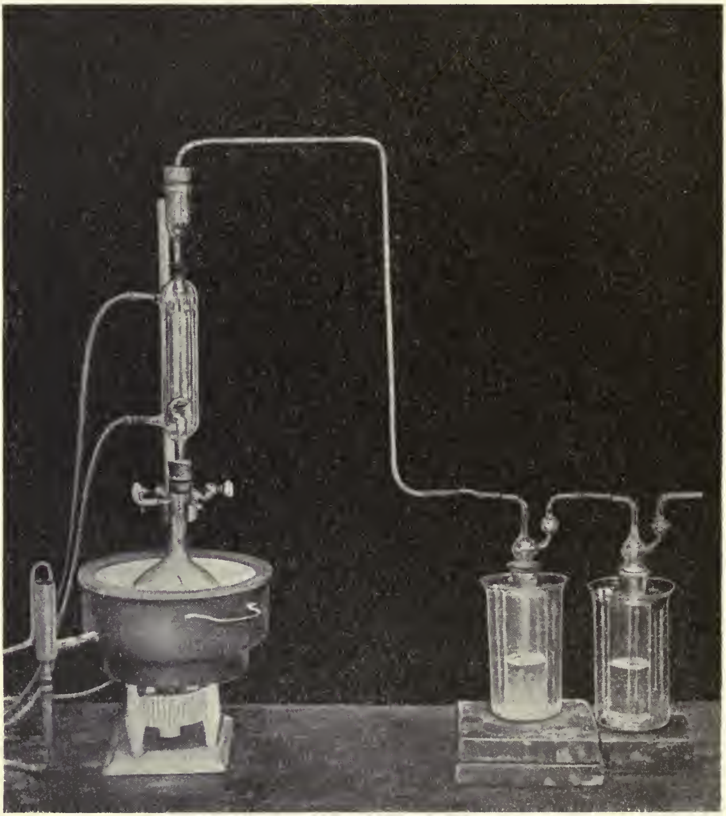


Fig. 95. Preparation of acetaldehyde. Distillation of the aldehyde and absorption in ether.

$$2AgNO_3 + H_2O + CH_3 \cdot CHO \rightarrow CH_3 \cdot COOH + 2HNO_3 + 2Ag$$

Fehling's solution is often used as a test for certain substances which are good reducing agents, and is commonly used as one of the tests for aldehydes.

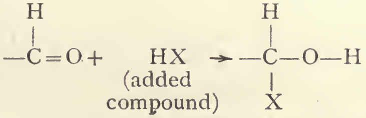
The solution is made in two parts: No. 1 Fehling's solution, consisting of a solution of copper sulphate, and No. 2 Fehling's solution, consisting of a solution of Rochelle salt (sodium potassium tartrate) made strongly alkaline with caustic soda. On mixing the two solutions, cupric hydroxide, $Cu(OH)_2$ or CuO, H_2O, is formed, but is held in solution by the tartrate, forming a deep blue liquid. The cupric hydroxide in solution is readily reduced by gently heating with an aldehyde, forming a red precipitate of cuprous oxide. The test is applied by mixing equal portions of Nos. 1 and 2 solutions, and adding 1 or 2 drops of formaldehyde solution and gently digesting in a hot water bath for some minutes.

$$2(CuO, H_2O) + CH_3 \cdot CHO \rightarrow CH_3 \cdot COOH + Cu_2O + 2H_2O$$

(2) Aldehydes are readily oxidised to acids, by the combination of an atom of oxygen with the aldehyde molecule, the atom of hydrogen in the aldehyde group being converted into the acidic hydroxyl, thus:

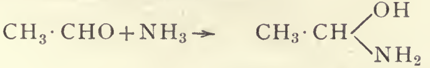
$$\underset{\overset{\|}{O}}{-C}-H \quad + O \quad \rightarrow \quad \underset{\overset{\|}{O}}{-C}-O-H$$

(3) Aldehydes form important addition or additive solid products by combination with (*a*) ammonia, (*b*) hydrocyanic acid, (*c*) sodium bisulphite, with the exception of formaldehyde which does not combine with ammonia to form such a compound. The molecules of the compound and the aldehyde combine together bodily, and it can be shown that in each case the oxygen in the aldehyde group is converted into hydroxyl, thus:



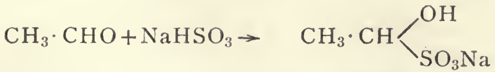
$$\overset{\overset{H}{|}}{-C}=O + \underset{\substack{\text{(added} \\ \text{compound)}}}{HX} \rightarrow \underset{\underset{X}{|}}{\overset{\overset{H}{|}}{-C}}-O-H$$

The following reactions take place between acetaldehyde and ammonia, hydrocyanic acid and sodium bisulphite.



acetaldehyde ammonia

ethylidene cyan-hydrin



acetaldehyde bisulphite

Formaldehyde hydrosulphites as discharging agents. Formaldehyde forms a series of compounds with the substances known as hydrosulphites (see Chapter XIX, p. 197), which are of importance in the textile industries and are largely used as reducing agents in indigo dyeing, etc., or as discharging agents in calico printing.

The compounds are stable, crystalline substances, similar in composition to the bisulphite compound described above, and as they are readily decomposed at steam heat, they liberate the hydrosulphite in the nascent condition, in which form it is extremely active as a reducing agent.

With sodium hydrosulphite, formaldehyde forms a substance $Na_2S_2O_4$, $2CH_2O$, $4H_2O$, put on the market by Meister, Lucius and Brüning under the name of **Hydrosulphite N.F.**, and by Casella's under the name **Hyraldite.** This substance has also been used as a detergent and bleaching agent.

This substance has been shown by Bernthsen to be a mixture of two compounds:

$NaHSO_3$, CH_2O, $2H_2O$ **Sodium bisulphite formaldehyde.**
$NaHSO_2$, CH_2O, $2H_2O$ **Sodium sulphoxylate formaldehyde.**

These are probably formed by the action of water on sodium hydrosulphite during the production of the formaldehyde derivative, thus:

$$Na_2S_2O_4 + H_2O \rightarrow NaHSO_2 + NaHSO_3$$

The two compounds may be separated by the solvent action of methyl alcohol, the bisulphite compound being less soluble and the sulphoxylate more soluble in the alcohol. The sodium sulphoxylate formaldehyde may thus be separated and is put on the market by the Badische Co., as **Rongalite C.**

These products, hyraldite and rongalite C, have recently been put on the market by Messrs Brotherton and Co. Ltd., as **Formosul.**

Both the bisulphite and sulphoxylate act as reducing agents by the withdrawal of oxygen from the compound reduced.

$$NaHSO_3 + O \rightarrow NaHSO_4$$
$$NaHSO_2 + O_2 \rightarrow NaHSO_4$$

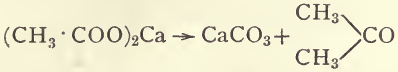
Sodium sulphoxylate, and the acid from which it is derived, sulphoxylic acid, H_2SO_2, have not been isolated.

Acetone. Acetone is the only member of the ketone group which need be dealt with here, but this compound is of importance owing to its solvent character.

Preparation. It is produced during the distillation of sugar, cellulose, etc., and is therefore formed in the distillation of wood.

As already mentioned under methyl alcohol this is one of the methods of obtaining it commercially, the acetone being extracted during the purification of the crude wood spirit in the production of pure methyl alcohol.

It is also obtained by a process of fermenting starch, and by the distillation of dry calcium acetate.



$$(CH_3 \cdot COO)_2Ca \rightarrow CaCO_3 + \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CO$$

Properties. Acetone is a colourless volatile liquid, boiling at 56° C., and mixes readily with water.

It is largely used in the manufacture of chloroform, iodoform, and other substances, and is employed in dissolving nitrocellulose in the production of celluloid and cordite.

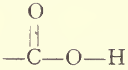
CHAPTER XXVI

THE FATTY ACIDS

FORMIC ACID AND FORMATES: ACETIC ACID AND ACETATES: PALMITIC AND STEARIC ACIDS: OILS, FATS AND WAXES: SAPONIFICATION: SOAPS: WOOL FAT, YOLK OR SUINT: WOOL GREASE, YORKSHIRE GREASE OR LANOLINE: ACID CHLORIDES AND ANHYDRIDES.

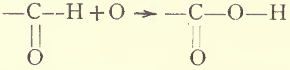
The organic acids derived from the paraffin hydrocarbons.

The organic acids, as already mentioned, contain the group of elements,



$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-H$$

known as the **carboxyl** group (—COOH), and this is formed by the oxidation of the aldehyde group, thus:



$$-\underset{\underset{\displaystyle O}{\|}}{C}-H+O \rightarrow -\underset{\underset{\displaystyle O}{\|}}{C}-O-H$$

Consequently, each aldehyde will give rise to a corresponding acid.

The lower members of the series, derived from the paraffin hydrocarbons, are strongly acid, but with increase in molecular weight the acidity is less marked, and the compounds assume more of the character of oils and fats.

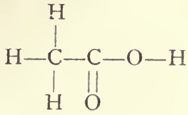
The compounds are present in animal and vegetable oils and in animal fats, the term, fatty acids, given to this series, being derived from this fact. The generic formula of the series is $C_nH_{2n}O_2$ or $C_nH_{2n+1}COOH$, the former giving the molecular formula only, whilst the latter gives the particular alkyl group in combination with carboxyl, though not giving the structure of the alkyl group.

All the acids are monobasic, the atom of hydrogen only in the carboxyl group being replaceable by metals with the formation of salts; the hydroxyl group in the carboxyl group may also be replaced by chlorine, giving rise to a compound known as an acid chloride, *e.g.*, acetyl chloride, $CH_3 \cdot CO(Cl)$.

Three hydrogen atoms in acetic acid may be gradually replaced by chlorine, giving rise to three chlor-derivatives, *viz.*, monochlor-acetic acid, $CH_2Cl \cdot COOH$; dichlor-acetic acid, $CHCl_2 \cdot COOH$; and trichlor-acetic acid, $CCl_3 \cdot COOH$, each of these acids being still monobasic in character.

All these facts point to the constitution of acetic acid being correctly represented by the formula:

$CH_3\cdot COOH$ or



$$\begin{array}{ccccccccc} & & H & & & & & & \\ & & | & & & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & \| & & & & \\ & & H & & O & & & & \end{array}$$

Fatty acids.

Name	$C_nH_{2n}O_2$	$C_nH_{2n+1}COOH$	M. P.	B. P.
Formic acid	CH_2O_2	$H\cdot COOH$	8·3° C.	101° C.
Acetic acid	$C_2H_4O_2$	$CH_3\cdot COOH$	17° C.	118° C.
Propionic acid	$C_3H_6O_2$	$CH_3\cdot CH_2\cdot COOH$	—	141° C.
Normal butyric acid	$C_4H_8O_2$	$CH_3\cdot CH_2\cdot CH_2\cdot COOH$	—	162° C.
Isobutyric acid	„	$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH\cdot COOH$	—	154° C.
Palmitic acid	$C_{16}H_{32}O_2$	$C_{15}H_{31}\cdot COOH$	63° C.	269° C.
Stearic acid	$C_{18}H_{36}O_2$	$C_{17}H_{35}\cdot COOH$	69° C.	287° C.
etc.				

The specific gravity gradually decreases with increase of molecular weight, formic acid being 1·231 at 10° C., but above the C_3 compound they are less than that of water, and palmitic and stearic acids have a sp. gr. of 0·852 and 0·845 at their respective melting points.

General methods of preparation. The acids may be prepared: (1) by the formation of an alkyl cyanide from an alkyl iodide and potassium cyanide, the cyanide being afterwards hydrolysed by heating with a solution of caustic potash, the following actions taking place:

$$CH_3I + KCN \rightarrow \underset{\text{methyl cyanide}}{CH_3\cdot CN} + KI$$

$$\underset{\text{(hydrolysis)}}{CH_3\cdot CN + 2H_2O} \rightarrow \underset{\text{acetic acid}}{CH_3\cdot COOH} + NH_3$$

The acetic acid forms the potassium salt by combination with the KOH. It should be noted that all organic cyanides can in this way be hydrolysed to a corresponding organic acid, the cyanide group, —CN, being converted into the carboxyl group, —COOH.

(2) By the action of CO on an alcoholate, or in the case of formic acid, caustic soda is used, thus:

$$\underset{\text{sodium methylate}}{CH_3ONa + CO} \rightarrow \underset{\text{sodium acetate}}{CH_3\cdot COONa}$$

(3) By the oxidation of an alcohol or an aldehyde, thus:

$$CH_3\cdot CH_2\cdot OH + O_2 \rightarrow CH_3\cdot COOH + H_2O$$

or

$$CH_3\cdot CHO + O \rightarrow CH_3\cdot COOH$$

Formic acid.

Preparation. Formic acid may be obtained by a great variety of methods, and was prepared over 200 years ago by the distillation of red ants. It also occurs naturally in stinging nettles, fir cones, etc.

It may be obtained by the general methods already described:

(1) Hydrocyanic acid ("prussic acid"), HCN, is hydrolysed by heating in a sealed tube with KOH:

$$HCN + 2H_2O \rightarrow H \cdot COOH + NH_3$$

(2) The second general method is used for the manufacture of formic acid, CO being passed over caustic soda, or soda lime, heated to 200° C.

$$NaOH + CO \rightarrow H \cdot COONa$$

(3) Methyl alcohol and formaldehyde when oxidised give formic acid.

(4) For laboratory purposes it is readily prepared by distilling a mixture of oxalic acid ($H_2C_2O_4$) and glycerol, the oxalic acid breaking up, thus:

$$\begin{array}{l} COOH \\ | \\ COOH \end{array} \rightarrow H \cdot COOH + CO_2$$

Actually, other complex actions take place between the glycerol and the oxalic acid forming ethereal salts, which are decomposed and hydrolysed, the ultimate products being formic acid and carbon dioxide, and the re-formation of the glycerol.

The action is best carried out by distilling 50 grams of oxalic acid and 40 c.c. of glycerol in a retort, with a thermometer dipping down into the glycerol, and the neck of the retort connected to a condenser. The distillation is carried to 110° C., until no more CO_2 is evolved, and another 50 grams of oxalic acid is added, and the distillation continued as before. The operation may be repeated, adding 50 grams of oxalic acid each time, until sufficient formic acid has been obtained.

The acid is purified by heating with an excess of lead carbonate, filtering, evaporating, and crystallising the lead formate, the dry salt being afterwards decomposed by heating to 110° C. in a stream of dry sulphuretted hydrogen:

$$(H \cdot COO)_2Pb + H_2S \rightarrow PbS + 2H \cdot COOH$$

Properties. Formic acid is a colourless liquid, boiling at 101° C., and has a powerful pungent odour. In a pure state it readily blisters the skin, and is used as an antiseptic.

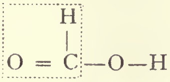
The acid is decomposed when heated with concentrated sulphuric acid, liberating pure carbon monoxide.

$$H_2SO_4 + H \cdot COOH \rightarrow CO + H_2SO_4, H_2O$$

It acts as a reducing agent, readily converting mercuric oxide into metallic mercury, reducing silver salts, etc., thus:

$$H \cdot COOH + HgO \rightarrow Hg + CO_2 + H_2O$$

The reducing character is accounted for by the formic acid containing the aldehyde group in its constitution :



$$\begin{array}{l} \phantom{O = {}}H \\ \phantom{O = {}}| \\ O = C-O-H \end{array}$$

The formates are stable compounds, but are crystallised with difficulty, the lead and copper formates being among those most easily crystallised.

Formic acid is sometimes used in place of acetic acid in dyeing operations.

Acetic acid, $CH_3 \cdot COOH$.

Preparation. Acetic acid may be obtained by the general methods already detailed (see p. 265).

It is obtained commercially as a by-product in the distillation of wood during the manufacture of methyl alcohol, and is separated from the pyroligneous acid as calcium acetate, $(CH_3 \cdot COO)_2Ca$. The acid may be liberated from the calcium acetate by distillation with sulphuric acid.

On a commercial scale it is also prepared in the form of a dilute solution, known as "vinegar," by the further fermentation ("acetous fermentation") of alcoholic liquids by the action of an oxidising enzyme, **mycoderma aceti.**

This is carried out in tubs containing beechwood shavings impregnated with the ferment. New shavings are inactive, but rapidly become active by running a vinegar solution over them, and the alcoholic liquid in passing over the shavings is brought freely into contact with air passing through holes in the sides of the tubs.

Pure acetic acid is always obtained commercially, however, from pyroligneous acid, and is purified by distillation and by freezing, crystallising at 17° C. as **glacial acetic acid.**

Properties. Acetic acid is a strongly acid liquid, with a powerful pungent odour, boiling at 118° C. It freezes at 17° C., and, if pure, is solid in winter time. A small quantity of water, however, lowers the freezing point, preventing the freezing of the liquid at ordinary winter temperatures. The acid may be detected in a solution by the addition of ferric chloride, which forms the deep red soluble ferric acetate, and on digesting this liquid for some time below the boiling point of water, it gradually deposits an insoluble red basic ferric acetate. Acetic acid is used in wool and silk dyeing.

Acetates. Many of the acetates are of importance, and find useful applications in the textile industries.

Sodium acetate, $CH_3 \cdot COONa, 3H_2O$. Sodium acetate is prepared from sodium carbonate or hydroxide and acetic acid; it is used in calico printing and wool-dyeing.

Calcium acetate, $(CH_3 \cdot COO)_2Ca$. Calcium acetate is obtained by dissolving calcium carbonate in acetic acid. It is used in the preparation of acetone, in the manufacture of acetic acid, for the preparation of other acetates, and in alizarin red printing.

Lead acetate ("sugar of lead"), $(CH_3 \cdot COO)_2Pb, 3H_2O$, is obtained from lead monoxide (litharge) or lead carbonate and acetic acid. It is extremely poisonous, but has a sweetish taste. It is used in preparing aluminium acetate and also in the formation of **chrome yellow** ($PbCrO_4$).

Copper acetate, $(CH_3 \cdot COO)_2Cu$, prepared by dissolving copper oxide or carbonate in acetic acid, is used in blue printing and in calico printing. The basic acetate, $(CH_3 \cdot COO)_2Cu, Cu(OH)_2$, is known as **verdigris,** and is used as a pigment.

Ferrous acetate, "pyrolignite of iron" or "iron liquor." This is obtained by dissolving any form of scrap iron in commercial acetic acid, or is frequently prepared on a large scale by the addition of commercial calcium acetate, obtained from pyroligneous acid, to ferrous sulphate, the calcium sulphate being separated by settling or filtration.

$$(CH_3 \cdot COO)_2Ca + FeSO_4 \rightarrow (CH_3 \cdot COO)_2Fe + CaSO_4$$

It frequently contains impurities of sulphates, acetic acid and occasionally tarry products. If the liquor deposits a resinous substance on standing, it is not safe for mordanting, though the commercial pyrolignite of iron is preferable to the pure ferrous acetate as the oxidation of the iron is retarded in the crude iron liquor. It is largely used in silk and cotton dyeing as a mordant, and is the most important iron mordant for calico printing.

Aluminium acetate, "red mordant," or "red liquor," $(CH_3 \cdot COO)_3Al$. This is prepared by addition of alum, or aluminium sulphate, to lead acetate, the sulphate being preferably only partly precipitated, the liquid containing a double sulphate and acetate of aluminium, $Al_2(SO_4)_3, 4(CH_3 \cdot COO)_3Al$.

$$Al_2(SO_4)_3 + 3(CH_3 \cdot COO)_2Pb \rightarrow 2(CH_3 \cdot COO)_3Al + 3PbSO_4$$

This solution is used preferably in a highly concentrated form, and is employed in mordanting silk and in calico printing.

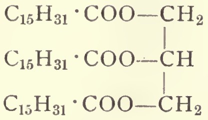
Other acetates used in printing or as discharging agents are **chromium acetate,** produced from chrome alum and lead acetate; and **tin acetate,** prepared from stannous chloride and lead acetate.

In using the above compounds as mordanting agents, acetic acid is driven off on heating, leaving aluminium or ferric oxides firmly adherent to the textile fibre, the oxides fixing the colouring matter when the material is dyed or printed.

Palmitic acid, $C_{15}H_{31}\cdot COOH$, and stearic acid, $C_{17}H_{35}\cdot COOH$.

Oils, fats and waxes. Palmitic and stearic acids are commonly occurring substances in nature, and, in combination with glycerol, are found in various animal fats, vegetable and animal oils and waxes. Thus, glycerol, which is a tri-hydric alcohol, combines with three molecules of a monobasic acid, such as palmitic or stearic acid, forming glyceryl palmitate (**palmitin**) and glyceryl stearate (**stearin**) in which the glyceryl radical ($C_3H_5\equiv$) takes the place of three acidic hydrogen atoms in the three molecules of acid, thus:

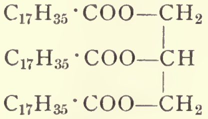
$(C_{15}H_{31}\cdot COO)_3C_3H_5$ or



$$\begin{array}{r@{}l} C_{15}H_{31}\cdot COO- & CH_2 \\ & | \\ C_{15}H_{31}\cdot COO- & CH \\ & | \\ C_{15}H_{31}\cdot COO- & CH_2 \end{array}$$

Palmitin or glyceryl palmitate,

and $(C_{17}H_{35}\cdot COO)_3C_3H_5$ or



$$\begin{array}{r@{}l} C_{17}H_{35}\cdot COO- & CH_2 \\ & | \\ C_{17}H_{35}\cdot COO- & CH \\ & | \\ C_{17}H_{35}\cdot COO- & CH_2 \end{array}$$

Stearin or glyceryl stearate.

In addition to these acids there is another acid, **oleic acid**, belonging to a series of compounds ($C_nH_{2n-1}COOH$) known as unsaturated compounds (see Chapter XXIX), which commonly occurs in oils, and in this case the acid contains less hydrogen than the fatty acids which are termed saturated acids, the formula of oleic acid being $C_{17}H_{33}\cdot COOH$. The glyceryl compound of this acid, glyceryl oleate (**olein**), $(C_{17}H_{33}\cdot COO)_3C_3H_5$, is found in many oils. Other saturated and unsaturated acids, *e.g.*, linoleic acid, $C_{17}H_{31}\cdot COOH$, ($C_nH_{2n-3}COOH$ series), which occurs as glyceryl linoleate in **linseed, cotton-seed and rape-seed oils**, glyceryl ricinoleate, $(C_{17}H_{32}(OH)\cdot COO)_3C_3H_5$, in **castor oil**, are less commonly found in oils, fats and waxes, and in some cases other alcohols are present, *e.g.*, cetyl alcohol, $C_{16}H_{33}\cdot OH$, which belongs to the alcohol series already described, is found as cetyl palmitate, $C_{15}H_{31}\cdot COOC_{16}H_{33}$, in **spermaceti wax. Bees' wax** and **carnauba wax**, used in dressings for textile materials, are similar compounds, these containing miricyl palmitate, $C_{15}H_{31}\cdot COOC_{30}H_{61}$, but the former also contains free cerotic acid, $C_{25}H_{51}\cdot COOH$. The three acids already mentioned, palmitic, stearic and oleic acids, may be looked upon as the most important of the compounds, and as typical of the others in oils and fats in combination with glycerol.

Beef and **mutton fat** consist largely of palmitin and stearin with some olein; **lard** is a similar mixture of compounds with a greater proportion of olein; **palm oil** is composed largely of palmitin, and **olive oil** of olein. **Cocoanut oil** contains the acids, $C_6H_{12}O_2$, caproic acid, $C_8H_{16}O_2$, caprylic acid, $C_{10}H_{20}O_2$, capric acid and $C_{12}H_{24}O_2$, lauric acid.

Hydrolysis and saponification of oils and fats. The above compounds containing an alcohol and an acid in combination, which are known as esters (see next chapter), are decomposed by the action of superheated steam, with the liberation of the free acid and the alcohol, and this action is termed **hydrolysis**, thus:

$$\underset{\text{"palmitin"}}{(C_{15}H_{31}\cdot COO)_3C_3H_5} + 3H_2O \rightarrow \underset{\text{palmitic acid}}{3C_{15}H_{31}\cdot COOH} + \underset{\text{glycerol}}{C_3H_5(OH)_3}$$

$$\underset{\text{"stearin"}}{(C_{17}H_{35}\cdot COO)_3C_3H_5} + 3H_2O \rightarrow \underset{\text{stearic acid}}{3C_{17}H_{35}\cdot COOH} + \underset{\text{glycerol}}{C_3H_5(OH)_3}$$

This action is made use of in **candle manufacture**, the mixture of stearic and palmitic acids after separation of oleic acid being known as **stearine.**

If, on the other hand, the ester is decomposed by the action of an alkali, such as caustic soda or potash, a soap is produced and the action is termed **saponification.** This term is also sometimes applied to the breaking up of the oil or fat by means of steam.

$$\underset{\text{"stearin"}}{(C_{17}H_{35}\cdot COO)_3C_3H_5} + 3NaOH \rightarrow \underset{\substack{\textbf{sodium stearate}\\ \text{or }\textbf{hard soap}}}{3C_{17}H_{35}\cdot COONa} + C_3H_5(OH)_3$$

Similar reactions take place in the case of palmitin and olein.

Saponification value or saponification equivalent. This action of saponification is made use of in the technical analysis of fats and oils, and in the valuation of these, a weighed quantity of the fat being heated with a measured quantity of a standard solution of potash dissolved in alcohol ("alcoholic potash"), and the amount of uncombined alkali is afterwards found by titration with a standard acid. From these figures, the amount of fat saponified by the molecular weight of the potash (56) is calculated, and this is the saponification equivalent.

Resinous and mineral oils and other fatty bodies, which are not saponified in this manner, are termed unsaponifiable matter.

In addition, however, to the determination of saponifiable and unsaponifiable matter, the oils and fats are valued by the determination of other physical and chemical characteristics, such as specific gravity, melting point, or solidifying point of fatty acids, iodine value, giving a measure of the amounts of unsaturated acids present from the quantity of iodine absorbed, etc.

Soap making. The saponification action is made use of in the manufacture of soap, suitable fats or oils being heated with alkalis to form the sodium or potassium salts of the fatty acids, the former giving rise to **hard soaps** and the latter to **soft soaps.**

In the **manufacture of a hard soap**, a suitable fat or oil is heated by steam in iron pans with caustic soda ("lye") until saponification is complete. Salt, in which the soap is insoluble, is then added, an operation termed "salting out," and the soap separates as a curd on the surface of the liquid. The liquid settling out below the soap, known as "spent lyes," contains the glycerol and salt, and is evaporated in vacuum pans for recovery of the salt by crystallisation and of the glycerol by distillation.

To produce a pure neutral curd soap, the soap is often redissolved in water, and the "salting out" process repeated.

In **making soft soaps**, olive oil, cotton-seed, linseed or other oils, are boiled with the required amount of caustic potash until saponification is complete. The finished soap after evaporation is run out, whilst still hot, into casks. As these soaps cannot be salted out by means of sodium chloride, owing to decomposition with the formation of a soda soap, they contain glycerol and usually caustic potash present in excess, etc., though on the continent potassium chloride has been used for "salting out" so as to produce a **neutral potash soap.**

Other substances are often added to household and toilet soaps, such as "water glass" (sodium silicate), borax, etc., but for textile purposes a pure soap is required, particularly for wool-washing, and one which is free from caustic alkali; in wool-washing the soap is generally mixed with a certain amount of soda ash (sodium carbonate or washing soda), the amount depending on the quality of the material.

In the analysis of soap (see Chapter XXXV, p. 321), the amounts of water, total alkali (combined and free alkali) and fatty acids (usually expressed as fatty anhydrides) are determined, whilst it may also be necessary to determine certain constants of the fatty acids, melting or solidifying point, molecular weight of the fatty acids, iodine value, etc., in order to determine the character of the oils from which the soaps have been manufactured.

Wool-fat, yolk or suint. The fat, which occurs in wool, known as wool-fat is not a true fat, as there are no glycerides present, the principal constituents being the alcohol, cholesterol ($C_{26}H_{44}O + H_2O$), isocholesterol, oleic acid, stearic and other free higher fatty acids.

The term suint or yolk is commonly used for substances extracted from wool in the washing process, though it is more correctly used for the fluid secreted in the skin of the sheep. It consists principally of potassium oleate, stearate, chloride, sulphate, with other fatty acids and mineral substances.

Wool grease, Yorkshire grease or lanoline. For the recovery of the grease after wool-washing the wash-liquors, containing soap, wool-fat, yolk, etc., are treated with sulphuric acid, a process termed "cracking," the fatty acids and oily matter coming up to the surface. The lower liquor is run off and the grease or "magma" is drained on canvas filters or is pumped into filter presses by compressed air, the grease being then liberated by treatment with steam. In the crude state, the grease, known as wool grease, Yorkshire grease or lanoline, forms a brown pasty mass. It consists essentially of free fatty acids, glyceryl compounds of the fatty acids, cholesterol, etc., though its composition varies considerably according to the kind of wool and its treatment. It may contain from 55 to 85 per cent. saponifiable matter, and from 8 to 40 per cent. unsaponifiable. It is used for the production of coarse soaps; and is also used for the manufacture of commercial oleic acid by distillation, producing hydrocarbon oils, by the decomposition of some of the fatty acids, **oleine** (commercial oleic acid), "stearin,".etc.

Acid chlorides.

When the acidic hydroxyl group in any of the fatty acids is replaced by an atom of chlorine, an acid chloride is obtained, thus:

$$\underset{\text{acetic acid}}{CH_3\cdot CO(OH)} \rightarrow \underset{\text{acetyl chloride}}{CH_3\cdot CO(Cl)}$$

The formation of this compound may be considered to be typical of this group of derivatives obtained from the fatty acids.

Preparation of acetyl chloride. 80 grams of phosphorus trichloride are gradually added from a dropping funnel to 100 grams of glacial acetic acid in a distilling flask immersed in a cold water bath. When the PCl_3 has been completely added, the liquid is heated to expel hydrochloric acid, the action being carried out in a fume cupboard, and the acetyl chloride is then distilled off on a rapidly boiling water bath.

$$PCl_3 + 3CH_3\cdot COOH \rightarrow 3CH_3\cdot COCl + P(OH)_3$$

Other secondary reactions also take place with the production of HCl.

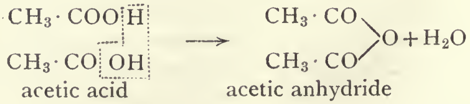
Properties. It is a colourless heavy liquid with a suffocating odour, B.P. 55° C. It reacts energetically with water, generating heat and forming acetic and hydrochloric acids.

$$CH_3\cdot COCl + H_2O \rightarrow CH_3\cdot COOH + HCl$$

It is used extensively in preparations of other organic compounds, and as a reagent in the preparation of acetyl derivatives for the detection of the number of —OH groups in alcohols.

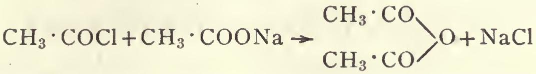
Acid anhydrides.

The organic acids give rise to anhydrides by the abstraction of water, thus acetic anhydride may be assumed to be obtained from 2 molecules of acetic acid by the withdrawal of water, thus:



$$\underset{\text{acetic acid}}{\begin{array}{l} CH_3\cdot COO\boxed{H} \\ CH_3\cdot CO\boxed{OH} \end{array}} \longrightarrow \underset{\text{acetic anhydride}}{\left.\begin{array}{l} CH_3\cdot CO \\ CH_3\cdot CO \end{array}\right\rangle O} + H_2O$$

Acetic anhydride or acetyl oxide. This is best prepared by the gradual addition of 50 grams of acetyl chloride to 70 grams of anhydrous sodium acetate in a retort, the mass being stirred when half the acid chloride has been added. The acetic anhydride may then be distilled off into a closed vessel with a drying tube attached, in order to prevent the moisture of the air coming into contact with the anhydride.



$$CH_3\cdot COCl + CH_3\cdot COONa \rightarrow \left.\begin{matrix}CH_3\cdot CO\\ CH_3\cdot CO\end{matrix}\right\rangle O + NaCl$$

Properties. It is a colourless liquid with a penetrating, pungent, suffocating, odour. B.P. 138° C. It readily combines with water and alcohols, thus:

$$(CH_3\cdot CO)_2O + H_2O \rightarrow 2CH_3\cdot COOH$$

$$(CH_3\cdot CO)_2O + C_2H_5OH \rightarrow CH_3\cdot COOH + \underset{\text{ethyl acetate}}{CH_3.COOC_2H_5}$$

CHAPTER XXVII

ETHEREAL SALTS OR ESTERS

NEUTRAL ESTERS AND ETHER ACIDS: ETHYL ACETATE:
FRUIT ESSENCES.

The acidic hydrogen in organic and inorganic acids may be replaced by alkyl groups giving rise to a series of compounds, known as ethereal salts, esters or compound ethers. The action may be brought about by the action of an alcohol on an acid, the reaction being similar, as already mentioned in the chapter on alcohols, to the action of an alkali on an acid.

In the case of polybasic acids, compounds may be obtained corresponding to both the acid and normal salts, and the ethereal salts are therefore divided into two classes:

(*a*) **Ether acids**, which still contain some of the acidic hydrogen, and correspond to inorganic acid salts.

(*b*) **Neutral esters**, in which all the acidic hydrogen is replaced by alkyl groups, corresponding to normal salts.

Ether acids. The ether acids are non-volatile compounds and are generally unstable. As an example of these, ethyl hydrogen sulphate or ethyl sulphuric acid, $C_2H_5HSO_4$, is obtained by mixing ethyl alcohol and sulphuric acid:

$$C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O$$

It is a syrupy liquid readily decomposed on heating into ethylene and sulphuric acid, and is also decomposed on heating with water or with alcohol (see preparation of ether, Chapter XXIV, p. 254).

Neutral esters. The neutral esters of the lower fatty acids are mostly volatile liquids with fruity odours, whilst the higher members are solids. The methyl, ethyl and propyl groups give neutral esters with lower boiling points than the acids contained in them, whilst the more complex alkyl groups give rise to compounds having a higher boiling point.

General methods of preparing neutral esters. These compounds are of much greater importance than the ether acids, and are prepared by the following general methods:

(1) By the action of alcohols upon acid chlorides, the following action taking place:

$$C_2H_5OH + \underset{\substack{\text{(acid chloride)}\\ \text{acetyl chloride}}}{CH_3\cdot COCl} \rightarrow \underset{\text{ethyl acetate}}{CH_3\cdot COOC_2H_5} + HCl$$

(2) By the action of a monohalogen derivative of a hydrocarbon upon the silver salt of an inorganic or organic acid, *e.g.*,

$$\underset{\text{silver acetate}}{CH_3\cdot COOAg} + \underset{\text{ethyl iodide}}{C_2H_5I} \rightarrow \underset{\text{ethyl acetate}}{CH_3\cdot COOC_2H_5} + AgI$$

(3) By the action of an alcohol upon an acid, as already mentioned. This reaction is, however, reversible, as it is a general property of the esters that they can be hydrolysed by water.

$$C_2H_5OH + CH_3\cdot COOH \rightleftarrows CH_3\cdot COOC_2H_5 + H_2O$$

The reversal of the reaction may, however, be prevented by the addition of sulphuric acid, and the reaction is then completed with the production of the ester.

Preparation of ethyl acetate or "acetic ether," $CH_3\cdot COOC_2H_5$.

The preparation of ethyl acetate may be looked upon as a typical preparation of an ethereal salt. 50 c.c. of ethyl alcohol and 50 c.c. of concentrated sulphuric acid are mixed in a distilling flask, and the mixture heated in an oil bath to a temperature of about 140° C. Equal volumes of alcohol and acetic acid are mixed in a separate tubulated bottle, and run into the flask as shown in Fig. 93, at approximately the rate at which the liquid is distilling over, the mixture being delivered nearly on to the surface of the liquid in the flask.

The following actions take place:

$$C_2H_5OH + H_2SO_4 \rightarrow \underset{\text{ethyl sulphuric acid}}{C_2H_5HSO_4} + H_2O$$

$$C_2H_5HSO_4 + CH_3\cdot COOH \rightarrow CH_3\cdot COOC_2H_5 + H_2SO_4$$

The sulphuric acid, being re-formed, will thus keep the action going continuously, and a large quantity of acetic acid and alcohol may be converted into ethyl acetate. The distillate contains a mixture of ethyl acetate, alcohol and acetic acid, and separates into two layers. It is purified by neutralising the upper layer with sodium carbonate in a porcelain dish, until the liquid no longer reddens blue litmus paper, and the layers are then separated in a tap funnel, the lower layer being neglected.

The upper layer is filtered, if necessary, through a dry filter, and then shaken up with a saturated solution of calcium chloride to remove alcohol, afterwards washed with water and dried with granular calcium chloride. The dry ethyl acetate may be finally redistilled and its boiling point taken.

Properties. Ethyl acetate is a volatile liquid, with a strong fragrant odour, B.P. 78° C. When heated with water, preferably in a sealed tube, the compound is hydrolysed, but is decomposed more readily by heating with caustic soda or potash (saponification).

Ethyl acetate has been used to a slight extent in textile work in detergents, on account of its good solvent power on resins.

Fruit essences. The esters are present in various fruits, and are now largely prepared for artificial fruit essences, *e.g.*, ethyl butyrate, $C_3H_7 \cdot COOC_2H_5$, has the odour of pineapple, amyl acetate, $CH_3 \cdot COOC_5H_{11}$, of pears, etc.

Glycerides of organic acids. The compounds dealt with in the last chapter (see Chapter XXVI, p. 269), under the heading of oils and fats, such as glyceryl stearate, palmitate, etc., belong to this group of compounds known as esters.

Butter contains 90 per cent. fat, which consists principally of glyceryl stearate, palmitate and oleate; about 7 per cent. of the fat consists of glyceryl butyrate and about 0·2 per cent. similar compounds of caproic, caprylic and capric acids.

Margarine consists of other fats derived from beef fat or suet, and various vegetable oils such as nut oils. It may be distinguished from butter by saponifying a little with alcoholic potash, heating to drive off the alcohol and acidifying with HCl to liberate the acid. In the case of butter, the unpleasant rancid odour of butyric acid will be observed.

CHAPTER XXVIII

NITROGEN COMPOUNDS

AMIDES : AMINES : NITRO-COMPOUNDS : CYANIDES : FERROCYANIDES : FERRICYANIDES : PRUSSIAN BLUE.

The nitrogen compounds may be considered to be principally derivatives of ammonia, in which the hydrogen is replaced either by an acid radical, such as acetyl, $CH_3 \cdot CO—$, or by an alkyl radical such as methyl.

The former of these compounds are known as **amides**, and the compounds may be produced by the reaction of ammonia with acid chlorides, thus from ammonia and acetyl chloride, acetamide is formed, thus :

$$CH_3 \cdot COCl + NH_3 \rightarrow \underset{\text{acetamide}}{CH_3.CO.NH_2} + HCl$$

The **amines**, on the other hand, are formed from ammonia by replacement of one or more atoms of hydrogen by alkyl groups, thus from ammonia, we may obtain primary compounds by replacement of one atom of hydrogen, secondary and tertiary compounds by replacement of two or three atoms of hydrogen respectively.

$$\underset{\text{ammonia}}{NH_3} \rightarrow \underset{\substack{\text{methylamine}\\ \text{(primary)}}}{NH_2 \cdot CH_3} \rightarrow \underset{\substack{\text{dimethylamine}\\ \text{(secondary)}}}{NH(CH_3)_2} \rightarrow \underset{\substack{\text{trimethylamine}\\ \text{(tertiary)}}}{N(CH_3)_3}$$

These compounds all possess properties similar to those of ammonia, in which the basic property of combining with acids to form salts is strongly marked.

In addition to the above, the basic amido group ($—NH_2$) may also replace hydrogen in the alkyl groups present in acids, forming compounds known as **amido-acids**, thus acetic acid gives rise to the compound amido-acetic acid, thus :

$$\underset{\text{acetic acid}}{CH_3 \cdot COOH} \rightarrow \underset{\text{amido-acetic acid}}{CH_2(NH_2) \cdot COOH}$$

Wool shows both acid and basic properties, and further appears to contain amido groups, so that it is possibly an amido-acid.

Nitro-compounds form another important series of nitrogen compounds, in which the monad nitro group, $—NO_2$, replaces H in the paraffin hydrocarbons or their derivatives, thus methane and ethane give rise to nitro-methane $CH_3 \cdot NO_2$ and nitro-ethane $C_2H_5 \cdot NO_2$.

These compounds are of lesser importance in the fatty series of organic derivatives, but important compounds of benzene and its derivatives are obtained by the introduction of the nitro group and will be referred to under benzene.

The nitro-compounds are readily converted into the basic amines by reducing agents :

$$\underset{\text{nitro-ethane}}{C_2H_5\cdot NO_2+6H} \rightarrow \underset{\text{ethylamine}}{C_2H_5NH_2} + 2H_2O$$

Cyanogen compounds. By the withdrawal of water from ammonium acetate by heating, acetamide is produced, and by the further withdrawal of a molecule of water by the action of a powerful dehydrating agent, an **alkyl cyanide** is formed, thus :

$$CH_3\cdot COONH_4 - H_2O \rightarrow CH_3\cdot CO\cdot NH_2$$
$$CH_3\cdot CO\cdot NH_2 - H_2O \rightarrow CH_3\cdot CN$$

Several compounds, which are of importance in textile industries, contain the cyanogen group, —CN, which in many ways acts like an atom of a halogen, such as Cl.

The group itself may occur in the free state as **cyanogen**, C_2N_2, which is prepared by heating mercuric cyanide, but care should be taken, as the gas evolved is very poisonous.

Hydrocyanic acid (prussic acid), HCN. This compound is also extremely poisonous, and the preparation of it should always be carried out in a good fume cupboard. It may be obtained by distilling potassium ferrocyanide with dilute sulphuric acid :

$$2K_4Fe(CN)_6 + 3H_2SO_4 \rightarrow 6HCN + 3K_2SO_4 + K_2Fe^{II}(Fe^{II}(CN)_6)$$

Cyanides. Hydrocyanic acid gives rise to an important series of compounds known as cyanides, the principal ones being the sodium and potassium salts, and by combination of these with other metallic cyanides, important double cyanides, such as potassium ferrocyanide (**yellow prussiate**) and potassium ferricyanide (**red prussiate**) are formed.

Potassium cyanide. This compound was originally made by Liebig's process in which potassium ferrocyanide was heated with potassium carbonate, but the product is very impure as large quantities of potassium cyanate, KCNO, are formed, thus :

$$K_4Fe(CN)_6 + K_2CO_3 \rightarrow 5KCN + KCNO + CO_2 + Fe$$

A purer product is obtained by heating potassium ferrocyanide alone to a bright red heat, or by heating dehydrated ferrocyanide of potash with sodium ; in the latter case the product obtained is a mixture of potassium and sodium cyanides.

$$K_4Fe(CN)_6 \rightarrow 4KCN + FeC_2 + N_2$$
$$K_4Fe(CN)_6 + 2Na \rightarrow 4KCN + 2NaCN + Fe$$

In **Beilby's process**, a mixture of potassium carbonate and carbon is heated to a red heat, and ammonia gas passed over the mixture, the mass being afterwards cast into rods or cakes.

$$K_2CO_3 + C + 2NH_3 \rightarrow 2KCN + 3H_2O$$

The compound is now also manufactured from ammonium thiocyanate, NH_4CNS, obtained by extracting cyanogen, during the purification of coal gas, by means of ammonium disulphide.

$$C_2N_2 + (NH_4)_2S_2 \rightarrow 2NH_4CNS$$

It is also obtained from **calcium cyanamide**, $CaCN_2$, prepared by heating calcium carbide (obtained by heating lime and carbon in an electric furnace) in an atmosphere of nitrogen in an electric furnace :

$$CaC_2 + N_2 \rightarrow CaCN_2 + C$$

The residue is heated with carbon and a suitable flux such as potassium carbonate in order to form KCN.

$$CaCN_2 + C + K_2CO_3 \rightarrow 2KCN + CaCO_3$$

Properties. Potassium cyanide is easily soluble in water, and is very poisonous.

It is largely used in electro-plating and electro-gilding for preparing soluble double cyanides of silver and gold, which are easily electrolysed depositing gold and silver :

$$AgNO_3 + KCN \rightarrow \underset{\text{curdy precipitate}}{AgCN} + KNO_3$$

$$AgCN + KCN \rightarrow \underset{\text{soluble double cyanide}}{AgCN, KCN}$$

It is also largely used in extracting gold from gold quartz.

Double cyanides.

Potassium ferrocyanide (yellow prussiate of potash), $K_4Fe(CN)_6, 3H_2O$.

This is an example of a soluble double cyanide similar to the one shown above, and may be prepared in a similar manner from a soluble ferrous salt by addition of potassium cyanide, until the precipitate which first forms is redissolved.

$$FeSO_4 + 2KCN \rightarrow \underset{\substack{\downarrow \\ \text{precipitate of ferrous cyanide}}}{Fe(CN)_2} + K_2SO_4$$

$$Fe(CN)_2 + 4KCN \rightarrow Fe(CN)_2, 4KCN \text{ or } K_4Fe(CN)_6$$

It is manufactured by heating nitrogenous refuse (such as blood, horn, hoofs, etc.) with potassium carbonate and iron filings in an iron pot. The mass is extracted with water and the ferrocyanide crystallised from the solution. It forms tabular yellow crystals, easily soluble in water.

The salt is used principally for the production of Prussian blue on cotton, wool and silk.

Potassium ferricyanide (red prussiate of potash), $K_3Fe(CN)_6$. This double salt is formed similarly to the ferrocyanide by the addition of potassium cyanide to a soluble ferric salt :

$$FeCl_3 + 3KCN \rightarrow Fe(CN)_3 + 3KCl$$

$$Fe(CN)_3 + 3KCN \rightarrow \underset{\substack{\downarrow \\ \text{red prussiate}}}{K_3Fe(CN)_6} \quad \text{or } Fe(CN)_3, 3KCN$$

It is usually manufactured, however, by oxidising potassium ferrocyanide by means of chlorine, then evaporating the solution and crystallising :

$$2K_4Fe(CN)_6 + Cl_2 \rightarrow 2KCl + 2K_3Fe(CN)_6$$

The compound crystallises in deep-red crystals, easily soluble in water.

It is used as a mild oxidising agent for aniline black, and as a discharge for indigo in an alkaline solution.

Prussian blue is formed by the addition of potassium ferrocyanide to a soluble ferric salt, the deep blue precipitate consisting of ferric ferrocyanide :

$$4Fe^{III}Cl_3 + 3K_4Fe^{II}(CN)_6 \rightarrow \underset{\substack{\downarrow \\ \text{ferric ferrocyanide (Prussian blue)}}}{Fe^{III}_4\{Fe^{II}(CN)_6\}_3} + 12KCl$$

In dilute solution, a deep blue liquid may be formed, as the Prussian blue is slightly soluble in water, but the substance may be salted out by the addition of salt.

Uses of potassium ferrocyanide and ferricyanide for detection of iron. Iron salts (-ous and -ic) may be readily detected in solution, or when mixed, by the use of ferro- or ferricyanide, the following being the reactions in a tabulated form.

Reagent	Fe (-ous)	Fe (-ic)
$K_4Fe(CN)_6$	Pale blue precipitate of potassium ferrous ferrocyanide $K_2FeFe(CN)_6$	Prussian blue precipitate of ferric ferrocyanide $Fe_4\{Fe(CN)_6\}_3$
$K_3Fe(CN)_6$	"Turnbull's blue" precipitate of ferrous ferricyanide $Fe^{II}_3(Fe^{III}(CN)_6)_2$	Brown coloration only

In the case of a ferrous salt, which is very liable to contain a trace of a ferric compound by oxidation of the iron compound, the presence of the ferric salt may be detected by adding potassium ferrocyanide and forming Prussian blue.

With a ferric salt, the presence of a trace of a ferrous compound may be detected by the addition of potassium ferricyanide forming the deep blue compound **Turnbull's blue.** Ammonium sulphocyanide (thiocyanate), NH_4CNS, may also be used to test for a trace of a ferric compound, the deep blood-red soluble **ferric thiocyanate** being formed if a ferric salt is present.

Potassium ferrocyanide, in the presence of acetic acid, is also a very sensitive test for copper, forming the chocolate-coloured precipitate of **copper ferrocyanide**, thus :

$$2CuSO_4 + K_4Fe(CN)_6 \rightarrow \underset{\text{copper ferrocyanide}}{Cu_2Fe(CN)_6} + 2K_2SO_4$$

In very dilute solutions a red-brown coloration may be obtained, and the reaction is used as a colour test for the estimation of minute quantities of copper compounds in solution.

CHAPTER XXIX

UNSATURATED HYDROCARBONS AND THEIR DERIVATIVES

ETHYLENE: CHLOR-DERIVATIVES OF ETHYLENE: ACETYLENE AND ITS CHLOR-DERIVATIVES: USE OF THE CHLOR-DERIVATIVES IN TEXTILE INDUSTRIES.

Ethylene.

The compound ethylene, C_2H_4, is the first member of the ethylene series of hydrocarbons, C_nH_{2n}, in which the various members forming the series are related to one another in a somewhat similar manner to the relations existing between the members of the methane series. The main point of difference in properties between these two series is, however, that the methane series, said to be saturated, can only form derivatives, such as chlor-derivatives, by replacement of hydrogen by chlorine, whereas the ethylene series of compounds, said to be unsaturated, may form with the halogens, halogen acids and other compounds, direct addition products without replacement of hydrogen.

From a consideration of all the properties of ethylene, the structure

$CH_2:CH_2$ or

$$\begin{array}{cc} H & H \\ | & | \\ C & = C \\ | & | \\ H & H \end{array}$$

is given to the molecule, and the double bond indicates its unsaturated character. Thus ethylene may combine with chlorine, a halogen acid, such as hydriodic acid, HI, or concentrated sulphuric acid directly to form addition products, and it is characteristic of these reactions that the ethylene always takes up two atoms of the halogen, or the equivalent, and passes into a saturated compound, thus:

$$CH_2:CH_2+Cl_2 \rightarrow \underset{\text{ethylene dichloride}}{CH_2Cl \cdot CH_2Cl}$$

$$CH_2:CH_2+HI \rightarrow \underset{\text{ethyl iodide}}{CH_3 \cdot CH_2I}$$

$$CH_2:CH_2+H_2SO_4 \rightarrow \underset{\text{ethyl sulphuric acid}}{CH_3 \cdot CH_2 \cdot HSO_4}$$

The higher compounds may be derived from the lower by substitution as in the case of the methane series, thus the second member propylene has the formula $CH_2 : CH \cdot CH_3$, obtained from ethylene by substituting a methyl group in place of an atom of hydrogen as detailed under the methane hydrocarbons. Similarly from propylene, there should be three butylenes possible, and three only are known. It should be specially noted that the double bond is merely a symbolical method of indicating unsaturation, and does not represent increased strength in that part of the molecule. The compound, if decomposed, is liable to split up at the double bond, showing that the affinity in the molecule is weaker rather than stronger at that point.

Preparation of ethylene. The compound may be obtained by heating ethyl alcohol with concentrated sulphuric acid, but as it is very liable to froth and char it is preferable to use syrupy phosphoric acid in place of sulphuric acid:

$$C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O$$
$$C_2H_5HSO_4 \rightarrow C_2H_4 + H_2SO_4$$
$$C_2H_5OH + H_3PO_4 \rightarrow C_2H_5H_2PO_4 + H_2O$$
$$C_2H_5H_2PO_4 \rightarrow C_2H_4 + H_3PO_4$$

The reaction is best carried out as shown in Fig. 96, the alcohol being dropped into 50 c.c. of syrupy phosphoric acid (sp. gr. 1·75) heated to 200° C. The acid is first heated, commencing to boil and giving

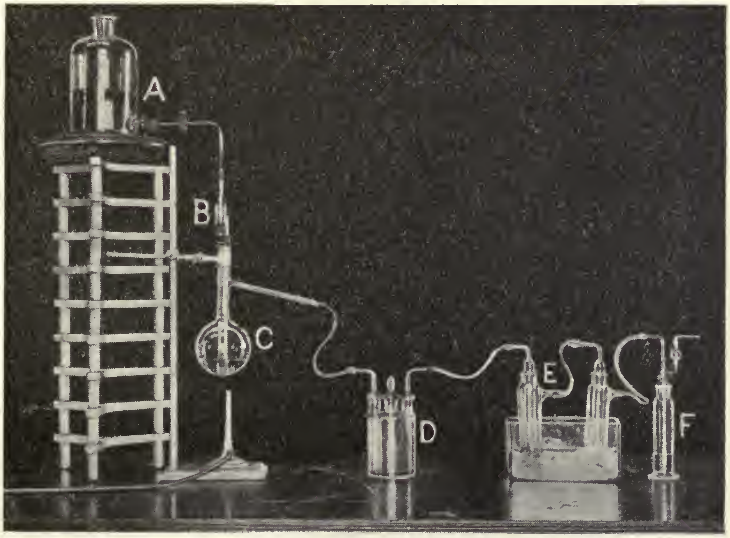


Fig. 96. Preparation of ethylene from alcohol and syrupy phosphoric acid, and conversion into ethylene dibromide. *A*, tubulated bottle containing alcohol; *B*, dropping tube; *C*, distilling flask containing syrupy phosphoric acid; *D*, trap bottle; *E*, bottles containing bromine; *F*, bottle containing caustic potash solution to absorb escaping bromine vapour.

off water at about 160° C., and the distillation is continued until the temperature shown by the thermometer immersed in the acid is 200° C., and the alcohol is then dropped at a suitable rate, which is regulated to give a steady stream of gas. In order to see the rate of dropping, the method shown in the sketch is employed, the alcohol being dropped from a tube inside a pipette and then delivered by the latter under the surface of the acid.

The reaction does not start unless a trace of a catalytic agent is present, such as about 1 grain of anhydrous zinc chloride, $ZnCl_2$, or a trace of mono-ethyl phosphoric acid, etc. Other more complex reactions take place than those indicated above, and traces of ether, etc., distil over and are caught in the Woulff's bottle. The ethylene may be collected over the pneumatic trough, or absorbed in liquid bromine, as shown, to form ethylene dibromide, until the liquid has lost its deep-red colour. The ethylene dibromide is afterwards washed with potash, water, dried with granular calcium chloride and distilled. B.P. 131° C.

Properties of ethylene. Ethylene is a colourless gas with a slight sweetish taste, and burns with a luminous flame, or forms an explosive mixture with oxygen.

$$C_2H_4+3O_2 \rightarrow 2CO_2+2H_2O$$

It is one of the chief illuminating constituents of ordinary coal gas. It readily combines with the halogens, halogen acids, and is readily absorbed by concentrated sulphuric acid.

Chlorine derivatives of ethylene. These compounds are of importance commercially as, like the chlorine derivatives of ethane, they are good solvents, with a good range in boiling point from volatile compounds boiling at 55° C. to less volatile liquids boiling at over 120° C. They are perfectly safe to handle, and being non-combustible they do not give off inflammable vapours, and in consequence they are also non-explosive. The compounds are employed as constituents of detergents, particularly in the manufacture of those of the "tetrapol" class.

Ethylene dichloride, $CH_2Cl \cdot CH_2Cl$, is a volatile liquid formed by direct addition of chlorine to ethylene, thus:

$$C_2H_4+Cl_2 \rightarrow C_2H_4Cl_2 \text{ or } CH_2Cl \cdot CH_2Cl$$

It is a colourless liquid, B.P. 84° C., with good solvent properties for resins, fats, etc.

Dichloro-ethylene, $CHCl:CHCl$, B.P. 55° C., sp. gr. 1·25, is very slightly soluble in water and has no action on metals. It is very suitable as a non-inflammable substitute for ether, particularly for extraction of oils.

Trichloro-ethylene, $CHCl:CCl_2$, B.P. 88° C., sp. gr. 1·47, is very slightly soluble in water, and has no anaesthetic properties; it is not attacked by alkalis and has no action on metals, though it has been stated that oils and fats extracted by trichloro-ethylene in iron vessels become coloured by iron. It forms a good substitute for benzene and carbon tetrachloride as a solvent for the extraction of oils and fats, giving no odour to the same. In the presence of moisture it forms hydrochloric acid.

Tetrachloro-ethylene, $CCl_2 : CCl_2$, B.P. 121° C., sp. gr. 1·62, is also a good solvent for oils and fats.

Acetylene, $CH \vdots CH$.

This compound belongs to a series of hydrocarbons more unsaturated still than the ethylene series, and is represented as shown with a triple bond indicating the unsaturated character. The generic formula of the series is C_nH_{2n-2}.

Preparation. It may be obtained by forming an electric arc between carbon poles in an atmosphere of hydrogen, an important synthesis, which is the starting point of many other syntheses.

It is also produced by the degraded combustion of other more saturated hydrocarbons, by limiting the supply of oxygen, and is formed in this way when a bunsen or Fletcher burner strikes back and burns at the base.

$$C_2H_6 + O_2 \rightarrow 2H_2O + C_2H_2$$

It may also be obtained by withdrawing hydrobromic acid (HBr) from ethylene dibromide by heating with an alcoholic solution of potash.

$$CH_2Br \cdot CH_2Br + 2KOH \rightarrow 2KBr + 2H_2O + CH \vdots CH$$

The usual method of preparing it commercially is from calcium carbide, obtained by heating a mixture of lime and carbon in an electric furnace.

$$CaO + 3C \rightarrow CaC_2 + CO$$

The calcium carbide is acted upon in the cold by water in suitable generators, acetylene being liberated with the generation of a considerable quantity of heat.

$$CaC_2 + 2H_2O \rightarrow CaO,\ H_2O + CH \vdots CH$$

Properties. Acetylene is colourless and possesses an unpleasant odour. It is very readily soluble in acetone under pressure, and this is taken advantage of in storing the gas in cylinders under pressure. It burns with a very luminous flame, liberating soot if the supply of oxygen is limited, and is explosive when mixed with air or oxygen.

$$2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$$

By passing oxygen into an acetylene flame, an intensely hot reducing blowpipe flame is obtained, which is used in oxy-acetylene welding.

The compound, being unsaturated, readily forms addition products with halogens, halogen acids, etc., and with chlorine forms **dichloro-ethylene** and **tetrachloro-ethane**, already dealt with, which form good solvents in the textile industries for fats, oils, etc., and are used in detergents.

$$CH \vdots CH + Cl_2 \rightarrow CHCl : CHCl$$
$$CH \vdots CH + 2Cl_2 \rightarrow CHCl_2 \cdot CHCl_2$$

CHAPTER XXX

OTHER ORGANIC ACIDS USED IN THE TEXTILE INDUSTRIES

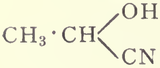
Lactic acid and lactates: Oxalic acid and oxalates: Tartaric acid and tartrates: Tartar emetic and tartar emetic substitutes as fixing agents in mordanting cotton: Citric acid: Oleic acid: Linoleic acid: Ricinoleic acid: Turkey red oil and its use in dyeing.

Lactic acid and lactates.

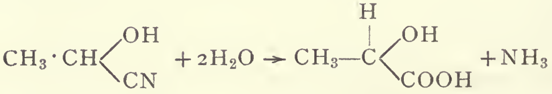
Lactic acid occurs in sour milk, and has been produced in this case by the lactic fermentation of sugars. Its formula $CH_3\cdot CH(OH)\cdot COOH$ indicates that it is a hydroxy-propionic acid, that is, propionic acid with one atom of hydrogen replaced by the hydroxyl group.

$$\underset{\text{propionic acid}}{CH_3\cdot CH_2\cdot COOH} \longrightarrow \underset{\text{lactic acid}}{CH_3\cdot CH(OH)\cdot COOH}$$

It may also be obtained by the hydrolysis of aldehyde cyanhydrin,



$CH_3\cdot CH\left\langle\begin{array}{l}OH\\CN\end{array}\right.$, thus :



$$CH_3\cdot CH\left\langle\begin{array}{l}OH\\CN\end{array}\right. + 2H_2O \rightarrow CH_3{-}\overset{\displaystyle H}{\overset{|}{C}}\left\langle\begin{array}{l}OH\\COOH\end{array}\right. + NH_3$$

The formula, as written in the equation, indicates that one of the carbon atoms is attached to four different groups and in such a case the carbon atom is said to be **asymmetric**. In all cases where an asymmetric carbon atom is present, the compound may take different isomeric forms, which are termed stereo-isomeric forms and the compound exhibits the property of **stereo-isomerism.**

In such an example as lactic acid, which is a simple case of stereo-isomerism, it is only possible to explain the property by assuming a space arrangement of the groups, the carbon atom being supposed to be within a tetrahedron and the four bonds directed towards the four corners of the tetrahedron. The two forms are then mirrored reflections one of the other, and are related to one another as the object is to its image in the mirror. Just as in the reflection of a person in a mirror, the right hand of the person appears as the left hand in the image, so one of the formulae may be termed a right-handed one and the other a left-handed form. This is illustrated in Fig. 97.

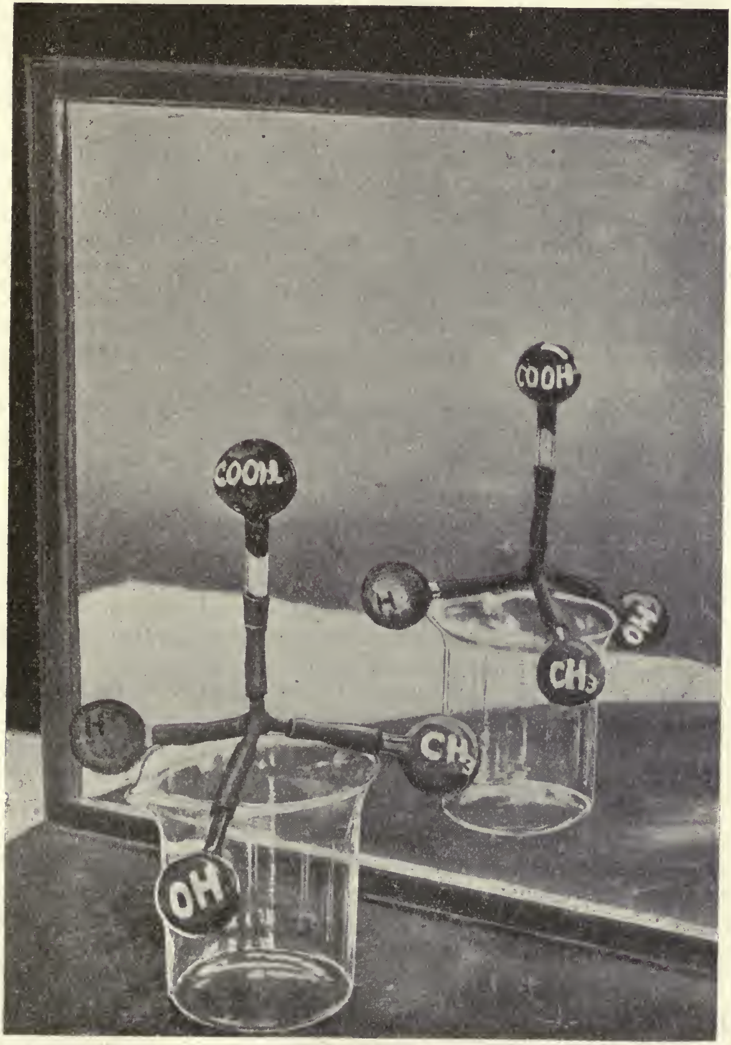
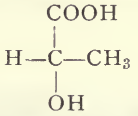
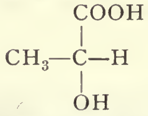


Fig. 97. Showing the stereo-isomerism of the lactic acid molecule. The groups (CH_3), (OH) and H, taken in this order are righth-anded or clockwise, but in the reflection in the mirror are left-handed or anti-clockwise.

The formula may be represented on a flat surface thus:



$$\begin{array}{c} COOH \\ | \\ H-C-CH_3 \\ | \\ OH \end{array}$$



$$\begin{array}{c} COOH \\ | \\ CH_3-C-H \\ | \\ OH \end{array}$$

In these two forms it will be noticed that taking the groups in the order COOH (1), CH_3 (2), OH (3), H (4), we pass in a clockwise direction in the case of the formula on the left, and in an anti-clockwise direction in the one on the right.

Compounds occurring in this way in stereo-isomeric forms have similar properties, but differ in their action on polarised light, the compounds in solution, when polarised light is passed through them, rotating in the one case the plane of polarisation to the right (the dextro- or *d*-compound) and in the other case to the left (the laevo- or *l*-compound).

The lactic acid present in sour milk has, however, no action on polarised light, due to the fact that it consists of both compounds, and one compensates the other in the action on polarised light, or it is said to be optically inactive.

The compound may be resolved, however, into its optically active constituents by crystallising its salts, and when these are carefully examined, although they may belong to the same crystalline system, yet there will be found to be developed on the crystals small faces which have the relationship of object and mirrored image to each other.

The *d*-lactic acid, known also as para- or sarco-lactic acid, is present in extract of meat from which it may be separated.

The ordinary lactic acid is inactive and may be produced by the fermentation of sugar by the lactic acid ferment, preferably in the presence of zinc oxide at about 34° C. Zinc lactate is formed, and the free acid may be liberated by the action of sulphuretted hydrogen. When evaporated it forms a thick, hygroscopic, non-crystallising syrup, giving rise to definite salts such as zinc and calcium lactates,

$$(C_3H_5O_3)_2Zn, 3H_2O \text{ and } (C_3H_5O_3)_2Ca, 5H_2O$$

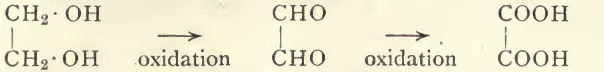
Lactic acid is used as an assistant in dichromate of potash baths for mordanting, and is put on the market in the form of zinc and antimony salts, generally combined in the latter case with free lactic acid. A double acid lactate of calcium and antimonyl (in which the monad antimonyl group, —SbO, takes the place of an atom of H) is put on the market as **antimonine**, and has approximately the following composition:

$$2SbO(C_3H_5O_3), Ca(C_3H_5O_3)_2, 2C_3H_6O_3$$

It contains 15 per cent. of Sb_2O_3, and is used as a substitute for tartar emetic as a fixing agent. The compound may be concentrated to a syrup without formation of a basic compound, and does not readily form a basic compound in solution. It is prepared by dissolving antimonious oxide, Sb_4O_6, in potassium acid lactate and then mixing with calcium lactate.

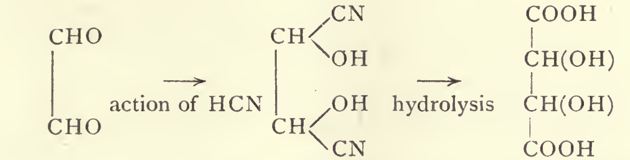
Dibasic and polybasic acids.

It has already been shown that monohydric alcohols give rise to fatty acids, and that the hydrocarbons give rise also to dihydric alcohols. These latter may give rise to dibasic acids such as oxalic and tartaric acids, *e.g.*,



$$\begin{array}{c}CH_2\cdot OH\\|\\CH_2\cdot OH\end{array} \xrightarrow[\text{oxidation}]{} \begin{array}{c}CHO\\|\\CHO\end{array} \xrightarrow[\text{oxidation}]{} \begin{array}{c}COOH\\|\\COOH\end{array}$$

glycol glyoxal (aldehyde) oxalic acid



glyoxal (aldehyde) glyoxal cyanhydrin tartaric acid

Oxalic acid, $\begin{array}{c}COOH\\|\\COOH\end{array}$, $2H_2O$. Oxalic acid is found in the cells of many plants, and may be obtained by heating cane sugar or sawdust with concentrated nitric acid.

It is manufactured by heating sawdust with a mixture of caustic soda and caustic potash on iron plates. The sodium and potassium salts are extracted, converted into calcium compounds, and the acid liberated by sulphuric acid.

Properties and uses.—Oxalates. The acid crystallises readily in prismatic forms with $2H_2O$, and it forms a series of well-defined salts. **Ammonium oxalate,** $(NH_4)_2C_2O_4$, H_2O, and **potassium oxalate,** $K_2C_2O_4$, H_2O, both readily soluble in water, and crystallising readily, are the principal compounds. The acid potassium compound crystallises as KHC_2O_4 or $K_2C_2O_4$, $H_2C_2O_4$, and also combines with free oxalic acid forming **potassium quadroxalate,** KHC_2O_4, $H_2C_2O_4$, $2H_2O$ or $K_2C_2O_4$, $3H_2C_2O_4$, $4H_2O$, known as **salts of lemon** or **salts of sorrel.** It is used for cleansing purposes, and for removing iron moulds and ink stains.

Oxalic acid is used in mordanting and calico printing, and as a detergent in combination with acetic acid. Chromic, stannic and stannous oxalates have also been suggested for use in calico printing, the latter for use as a discharging and reducing agent.

Antimony compounds, which do not readily form basic compounds, are put on the market as mordants for cotton, and for fixing basic dyes in combination with tannin, acting as substitutes for tartar emetic, but cannot replace this in all cases.

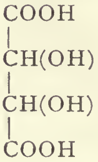
Patent antimony salt has the composition

$$SbF_3,\ 2Na_2C_2O_4,\ Na(SbO)C_2O_4,\ H_2O$$

and contains 41 per cent. of Sb_2O_3.

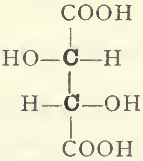
Antimony oxalate is a double oxalate of antimony and potassium, with the composition $K_2C_2O_4$, $KSb(C_2O_4)_2$, $6H_2O$. It is prepared by dissolving Sb_4O_6 in potassium hydrogen oxalate, and crystallises from water, in which it is easily soluble, in the form of fine needles. It gradually forms, however, a basic salt from a solution of the compound in water; the salt contains 23·7 per cent. Sb_2O_3.

Tartaric acid,



$$\begin{array}{l}\text{COOH}\\ |\\ \text{CH(OH)}\\ |\\ \text{CH(OH)}\\ |\\ \text{COOH}\end{array}$$

The molecule of this compound contains two asymmetric carbon atoms, shown centrally in heavy type in the following formula:

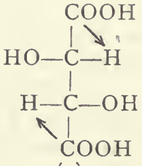


$$\begin{array}{c}\text{COOH}\\ |\\ \text{HO}—\mathbf{C}—\text{H}\\ |\\ \text{H}—\mathbf{C}—\text{OH}\\ |\\ \text{COOH}\end{array}$$

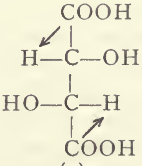
Thus each asymmetric carbon atom is combined with the four groups

—COOH, —H, —CH(OH)(COOH), and —OH

and considering each asymmetric carbon atom separately, the above groups are arranged in a clockwise direction around the carbon. The compound is therefore optically active. In addition we may obtain its mirrored reflection which may be shown diagrammatically thus:



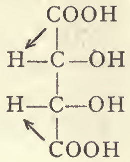
(1)



(2)

(mirrored reflection of (1))

In the image formula on the right, the groups around each asymmetric C, in the order given above, are arranged anti-clockwise, and this is also optically active. One of these compounds is termed **dextro-** (*d*-tartaric acid) and the other **laevo-tartaric acid** (*l*-tartaric acid), whilst the mixture of the two is termed **racemic acid**. In addition, however, a compound, **mesotartaric acid**, can be prepared in which one asymmetric carbon atom is dextro- and the second one laevo-, and the molecule, which is optically inactive, is then said to be internally compensated. This may be represented symbolically by the formula:



Taking again the groups

$$—COOH, —H, —CH(OH)(COOH), \text{ and } —OH$$

in this order, these are combined with the upper asymmetric carbon atom in an anti-clockwise direction, and with the lower carbon atom in a clockwise direction.

In the above explanation, the groups have been assumed to be laid out on a flat surface, but in reality the bonds should be directed towards the angles of two tetrahedra linked together by a common bond.

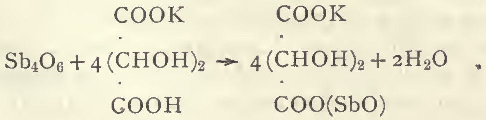
d-**Tartaric acid** is the compound found in nature in the form of the free acid, and as the acid potassium compound in grape juice. The potassium hydrogen tartrate crystallises during the fermentation as crude **argol**, a brownish powder, which is recrystallised to produce pure potassium hydrogen tartrate, $KHC_4H_4O_6$, known commonly as "cream of tartar." The acid is prepared from it by precipitating calcium tartrate by means of chalk, and decomposing the calcium salt by sulphuric acid. The acid crystallises well in prismatic forms, easily soluble in water and alcohol and melts at 205° C.

Tartrates. Potassium hydrogen tartrate or bitartrate (tartar or cream of tartar), $KHC_4H_4O_6$, is only slightly soluble in cold water but readily in hot. It is used as an adjunct in mordanting with potassium dichromate.

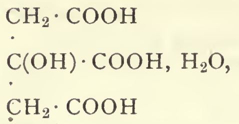
Rochelle salt is a double sodium potassium tartrate having the formula $NaKC_4H_4O_6, 4H_2O$.

Tartar emetic, potassium antimonyl tartrate, $2K(SbO)C_4H_4O_6, H_2O$, or sometimes written $K(SbO)C_4H_4O_6, \frac{1}{2}H_2O$, is an important material used in the textile industries, and in the form of a dilute solution (1 to 2 per cent. of tartar emetic) is used to fix tannin as antimony tannate for mordanting purposes on cotton.

It is prepared by dissolving antimonious oxide, Sb_4O_6, in cream of tartar and crystallising from the solution obtained.



$$Sb_4O_6 + 4\begin{array}{c}COOK\\ \cdot\\ (CHOH)_2\\ \cdot\\ COOH\end{array} \rightarrow 4\begin{array}{c}COOK\\ \cdot\\ (CHOH)_2\\ \cdot\\ COO(SbO)\end{array} + 2H_2O\ .$$



Citric acid, $C_6H_8O_7$, H_2O, or $\begin{array}{l} CH_2\cdot COOH \\ \vert \\ C(OH)\cdot COOH \\ \vert \\ CH_2\cdot COOH \end{array}$, H_2O, occurs naturally in lemons, oranges, and gooseberries, and is extracted from lemon juice by forming the calcium salt, and decomposing this by sulphuric acid. It is also obtained commercially by the fermentation of solutions of glucose by certain moulds.

The acid readily crystallises in large prisms easily soluble in water. It is used to some extent in silk dyeing for brightening, and in reserve printing.

Unsaturated acids.

Oleic acid, $C_{18}H_{34}O_2$, and **linoleic acid, $C_{18}H_{32}O_2$,** have been already dealt with under fats and oils, the former, belonging to the acids derived from the ethylene series, occurring principally in olive oil, and the latter, belonging to the acetylene series of acids, in linseed oil as glycerides. The latter oil belongs to a class known as drying oils which readily absorb oxygen from the air forming resinous bodies. Boiled linseed oil, produced by heating the oil with driers (metallic oxides such as litharge), is largely used in pigments, and in this form the oxidation is accelerated. This oxidising action produces heat with a resulting rise in temperature, and **spontaneous combustion of waste oily materials** may generally be traced to this action. **Oil cloth** is prepared by soaking canvas with linseed oil, and then oxidising, and **linoleum** is made from oxidised oil, cork and other similar substances.

Ricinoleic acid, $C_{18}H_{34}O_3$, is a hydroxy-acid derived from oleic acid by the replacement of H by the —OH group. It occurs in castor oil principally as the glyceride, and, if liberated by saponification, it may be obtained as a crystalline mass melting at 16° to 17° C.

Turkey red oil (alizarin oil, sulphated oil or soluble oil). This is prepared by adding 20 to 40 parts of concentrated sulphuric acid slowly to 100 parts of castor oil, and maintaining the temperature below 40° C. for about 18 hours, or until the product gives a clear solution when mixed with distilled water. It is then washed with brine to remove H_2SO_4, and neutralised by caustic soda or ammonia. Olive oil, cotton seed oil, rape seed oil, etc., are sometimes used for the preparation in place of castor oil, but do not yield so good a product, as these give saturated acids whilst good castor turkey red oil consists solely of unsaturated acids, the valuable portion of the oil consisting of ricinoleo-sulphuric acid or its salts.

It is very soluble in water, and the practical value of this substance is probably due to the action rendering castor oil soluble.

It is largely used in turkey red dyeing, as a mordant in cotton dyeing with basic colours, in calico printing and in the finishing of cotton goods. The alkaline solution of this substance acts as a soap, and may be used as such.

CHAPTER XXXI

THE CARBOHYDRATES

MONO- DI- AND POLY-SACCHAROSES: GLUCOSE: CANE SUGAR: STARCH: CELLULOSE: DEXTRIN: GUMS: USES OF THESE IN THE TEXTILE INDUSTRIES.

The carbohydrates contain the elements carbon, hydrogen and oxygen only, and the last two elements are always present in the proportion to form water. The compounds are oxidation products of the higher polyhydric alcohols, and are either aldehydes or ketones, but at the same time contain the alcohol group (—OH) and have the properties of alcohols.

The compounds are therefore termed **aldoses** or **ketoses**, according to the group present, either aldehyde or ketone.

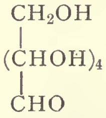
Most of the compounds occur in vegetable or animal life, and may be classified into the **sugars**, which are sweet crystalline bodies, and the substances of the starch and cellulose family which are non-crystalline, without taste, and have an organised structure. The sugars are further subdivided into two groups, and the usual classification adopted is **monosaccharoses**, C_5 or C_6 compounds, the **disaccharoses**, C_{12}, C_{18} or C_{24} compounds, and the **polysaccharoses**, the $(C_6)_n$ compounds. The following compounds will be dealt with as important ones in the textile industries, though as most of the compounds are optically active there are many stereo-isomeric forms, and these must be looked upon as typical compounds only.

Carbohydrates.

Sugars		Starch family
Monosaccharoses (hexoses) $C_6H_{12}O_6$	Disaccharoses $C_{12}H_{22}O_{11}$	Polysaccharoses $(C_6H_{10}O_5)_n$
Glucose (dextrose or grape sugar) Fructose (fruit sugar or laevulose)	Cane sugar (or sucrose)	Starch, cellulose, dextrin, gums

Monosaccharoses.

Glucose, dextrose or grape sugar. The formula of this compound is



$$\begin{array}{c} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CHO \end{array}$$

It occurs naturally in the vegetable kingdom and is present in ripe grapes. It may be obtained mixed with fructose as already detailed in the chapter on alcohols (see Chap. XXIV), by the hydrolysis of cane sugar, the latter being heated with a small quantity of mineral acid, such as HCl:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

It is obtained on a large scale in a similar manner from starch by hydrolysing with dilute sulphuric acid, the following action taking place:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$$

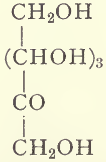
Chalk is added to neutralise the acid, the liquid filtered through animal charcoal to decolorise it, evaporated in vacuum pans and solidified.

Glucose in its usual form is a pale yellowish mass, but may be crystallised in six-sided plates melting at 86° C. It is readily soluble in water, the solution rotating the plane of polarisation of polarised light to the right (dextro-rotatory). The strength of a solution is often found polarimetrically by this method in instruments known as **polarimeters.**

It acts as a reducing agent, reducing ammoniacal silver nitrate solution and Fehling's solution. The last method is also made use of for estimating glucose by the amount of cuprous oxide which is produced by reduction.

Glucose is used in calico printing as a discharging agent, and for fixing indigo on the fibre in printing by the Schliefer and Baum glucose method.

Fructose, fruit sugar or laevulose is a ketonic compound of the formula



$$\begin{array}{c} CH_2OH \\ | \\ (CHOH)_3 \\ | \\ CO \\ | \\ CH_2OH \end{array}$$

and occurs both as a dextro- and laevo-rotatory compound.

Disaccharoses.

Cane sugar or sucrose, $C_{12}H_{22}O_{11}$, is found in beet root and in the sugar cane, from which it is extracted. It readily crystallises in prisms, melting at 160° C. The solution is dextro-rotatory, and the strength of a solution may be found polarimetrically by making use of this property. It is readily hydrolysed as already described into dextrose and fructose, or into the latter principally if sulphuric acid is used. When hydrolysed, the mixture of dextrose and fructose is sometimes termed "invert sugar." Cane sugar has no action on Fehling's solution, but reduces it after inversion.

Polysaccharoses.

Starch, $(C_6H_{10}O_5)_n$. The formula of starch indicates that its molecular weight is not known, but the value of n is probably very high. It is found in most forms of plant life, more particularly as microscopic grains, which are enclosed in cells, in the roots, root-nodules, pith, and fruits, making its appearance most abundantly towards the end of the vegetative period.

For technical purposes, and for a **dressing agent**, it is principally obtained from wheat, maize, rice, potatoes, etc.

It is prepared by softening the material in running water, after which it is ground and again washed in running water, the material at the same time being sieved to separate cellulose, or the material of the cell wall, etc. The milky liquid is settled, and the sediment is further washed repeatedly to remove fibrous material. In the case of maize, rice, and wheat starch, it is treated with a dilute solution of caustic soda, again washed, the greater portion of the water extracted in a centrifugal separator and dried.

The compound is a white uncrystallised solid, the grains being granular and exhibiting under the microscope a series of concentric rings. The grains vary in shape and size, and the position of the nucleus varies in different starches.

The compound is almost insoluble in cold water, but when it is heated the cells burst, forming a liquid, which, on cooling, gives a jelly known as starch paste. The material should be tested for grit, especially if it is to be used in calico printing, by making a thin paste on a white tile and testing for grit with the flat portion of a spatula.

The starch paste or solution in water gives a deep blue coloration with iodine, but if the liquid is heated the colour disappears, returning on cooling. The blue iodide of starch, which is formed, is an extremely unstable body, and starch should not be tested in this way in the form of a hot solution.

By heating starch with steam or water under pressure, it is converted into a soluble form known as **soluble starch.** It will dissolve in hot water but is deposited as an amorphous white powder on cooling. The molecular weight of this form has been determined, and the value of n in the above formula is said to be 200. The soluble starch is suitable for sizing and for the finishing of yarns and fabrics, serving well as a thickening material.

By heating starch with dilute acids, dextrin $(C_6H_{10}O_5)_n$ is formed, and finally glucose. By the action of diastase at 60° C., it is converted into dextrin and maltose ($C_{12}H_{22}O_{11}$, similar to cane sugar).

Cellulose, $(C_6H_{10}O_5)_n$. There appear to be several different varieties of cellulose, probably differing in the value of *n* in the above formula, and these yield different products on hydrolysis, but the name is applied to the compound forming the principal constituent of plant tissues, and this is closely allied to starch. Cotton is one of the purest natural forms, and pure cellulose may be obtained from cotton wool by extraction with caustic soda, then hydrochloric acid, and washing successively with water, alcohol and ether. The special filter papers, which have been treated with hydrochloric acid, or as above with acids, water, alcohol and ether, are almost pure cellulose, and leave only a minute trace of ash on burning.

Properties of cellulose. It is a white amorphous powder when in the pure state, very inert to reagents, and with neither acidic nor basic properties. It is not changed on heating to 100° C., but continued heating at 150° C. gradually turns it brown and brings about decomposition. It is very hygroscopic, and, after drying thoroughly, readily takes up moisture from the atmosphere. It is insoluble in boiling water, but at higher temperatures under pressure it decomposes, and passes into solution in water.

Dilute acids and alkalis have no effect upon it, and although the compound resists the action of oxidising agents to a considerable extent, yet when heated with dilute nitric acid, chromic acid, etc., or with strong solutions of bleaching powder, an oxidising action takes place and a substance termed **oxy-cellulose** is formed. The strength of the fibre is very considerably diminished in consequence, and as the oxy-cellulose has a marked affinity for basic dyes its presence is liable to give rise to unevenness in dyeing. The accidental production of this body in treatment of cotton is a frequent cause of defects.

Cellulose is soluble in an ammoniacal solution of cupric oxide (**Schweitzer's reagent**), the reagent being best formed by blowing air through a mixture of copper filings and strong ammonia. In this reagent the cellulose swells up, then gelatinises and finally dissolves. It may be precipitated from the blue liquid by dilution, or by the addition of dilute acids, as a gelatinous mass, this action forming the basis of one of the methods of producing artificial silk.

Willesden canvas is formed by rapid treatment of woven material with the above copper reagent, thus acting upon the cellulose on the surface only, so that when the material is dried over cylinders the surface fibres are welded together making it waterproof. **Willesden paper** is produced in a similar manner rendering the paper waterproof.

One part by weight of fused zinc chloride dissolved in two parts of strong hydrochloric acid is also a good solvent for cellulose, dissolving it almost instantly without change.

Action of acids and alkalis on cellulose. Mineral acids in a very dilute form, as already mentioned, have no action on cellulose, but concentrated sulphuric acid causes it to swell up into a gelatinous mass, and dilution with water precipitates **amyloid**, a modified cellulose. This action is used for the production of **parchment paper**, which is grease-proof, by treating unsized paper superficially with sulphuric acid (sp. gr. 1·67) for a few seconds, then washing and drying. If the action of the concentrated acid is allowed to continue, the amyloid is converted into dextrin.

The action of moderately concentrated acids appears to be one of hydration, in which water is taken up by the cellulose forming **hydrocellulose** $(C_6H_{10}O_5)_n + xH_2O$. The formation of this body forms the basis of carbonisation and the production of parchment paper. Hydrocellulose is turned blue by iodine, whereas cellulose is unstained, and this reaction may be obtained with parchment paper. By boiling with acid the hydrocellulose is gradually converted into glucose.

It is important in bleaching and dyeing that the formation of hydrocellulose should be avoided.

Non-volatile organic acids act upon cellulose similarly when heated, and consequently the material after treatment with these should be well washed before drying; formic and acetic acids volatilise on heating and have no action on the cellulose.

The action of zinc chloride on cellulose is very similar to that of a mineral acid.

Cellulose when treated with strong nitric acid, or with a mixture of sulphuric and nitric acids, gives rise to a series of so-called **nitro-celluloses,** which are nitrates of cellulose. The bodies are insoluble in water and alcohol, but soluble in a mixture of ether and alcohol, the lower nitrates being dissolved in this mixture to form **collodion.**

If the liquid is forced into water through fine capillary tubes, lustrous silky fibres are obtained, a method which is used for the production of **artificial silk.** It is denitrated by the action of ammonium sulphide to render it non-explosive. Tenacious films for photographic films and papers are also produced from collodion.

Gun-cotton is a hexanitrate of cellulose, and after dissolving in acetone is mixed with nitro-glycerine to form **cordite.**

Alkalis in a dilute condition have little action on cellulose if air is excluded, but in the presence of air oxy-cellulose is formed. With strong alkalis, however, a remarkable change takes place. When applied to cotton, the structure of the fibre is considerably modified, the walls of the fibre becoming thicker, and if applied to cloth there is a contraction in length and breadth, whilst the substance becomes thicker, stronger and translucent. If the cellulose is afterwards washed, it is permanently hydrated by the formation of a definite compound with water, probably forming hydrocellulose.

The amount of contraction varies with the conditions, but may be as much as 20 per cent., and the tensile strength is similarly increased. The increase in weight, due to the formation of the hydrate, is about 5 per cent. At the same time the material has also an increased affinity for dyestuffs. The process is used for the production of crinkled surfaces or **crape** effects on cotton goods, but if the material is maintained under tension to prevent contraction, and washed whilst still under tension, the material does not afterwards take the crepon effect, though it acquires a silky lustre, a process known as **"mercerisation" of cotton.**

Dextrin or British gum. Dextrin is prepared either by roasting dried starch to about 250° C., or by treatment of starch with dilute sulphuric acid, or by partially hydrolysing the starch with diastase for about twenty minutes at about 70° C. It is then boiled, cooled, filtered and evaporated to dryness.

It forms a yellowish powder, soluble in water, and gives a red colour with iodine solution. It is sold in several grades, the "dark" gum being unsuitable for most purposes, and may contain as impurities, starch, dextrose, sand, gypsum, etc., the percentage of dextrin in commercial samples varying from about 50 per cent. to 70 per cent. British gum is used in printing and finishing fabrics, and for dressing crape, lace, etc.

Gums. The term gum is used for vegetable substances resembling gum arabic, swelling up in water to a thick jelly, from which alcohol will precipitate the gum. They are glassy transparent substances exuding from certain plants, and must first be converted into dextrin before they form sugars.

The principal gums in use in the textile industries are **gum arabic**, occurring in commerce as nearly white, irregularly-rounded, brittle lumps; **gum senegal**, forming larger spherical lumps, dull on the exterior like etched glass, but transparent in the interior, and white to reddish-yellow in colour; **gum tragacanth**, in the form of thin, irregular, flat, yellowish-white masses, which are horny in character and difficult to powder.

These gums are used in printing and finishing as adhesive dressings or thickeners.

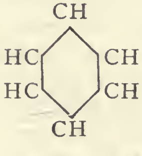
CHAPTER XXXII

THE BENZENE DERIVATIVES

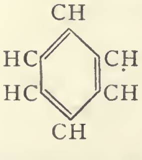
BENZENE: TOLUENE: XYLENE: NITRO- AND SULPHONIC ACID DERIVATIVES: NITROBENZENE: ANILINE AND ITS SALTS: PHENOL OR CARBOLIC ACID: BENZOIC ACID: SALICYLIC ACID: TANNIC ACIDS: USE OF TANNIN MATTERS IN THE DYEING INDUSTRY.

It is impossible in the scope of this work to give more than a very elementary notion of the benzene compounds, as these are so numerous and complex, and some branches of these compounds, such as the dye-stuffs, require separate treatises.

Benzene and its ring structure. Benzene is the simplest of the derivatives, generally known as aromatic compounds, and has the formula C_6H_6, being the first member of a series of hydrocarbons of the generic formula C_nH_{2n-6}. From a study of the properties of these compounds, and the fact that the simplest compound contains six atoms of carbon, Kekulé founded his theory of the benzene ring in which the carbon atoms are represented as attached in a closed chain or hexagon, thus:

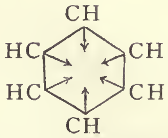


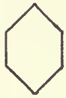
This formula does not account for the fourth valency of the carbon atom, but Kekulé accounted for this by an alternate double bond, thus:



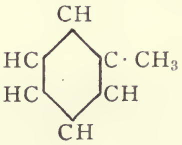
This would indicate, however, the presence of the ethylene linkage, with consequent unsaturated properties, whereas the properties of the benzene series of hydrocarbons are very different from the general properties of unsaturated hydrocarbons.

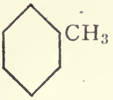
Other modes of disposing of this fourth valency have been suggested, such as the centric formula of Armstrong



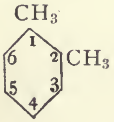
but until more is known of the subject it is usual to write the formula simply as a hexagon , often without putting in the carbon and hydrogen atoms.

Toluene and xylenes. The second member of the series is toluene or methyl benzene, and its formula may be derived from benzene by substitution, thus

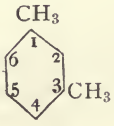
$C_6H_5 \cdot CH_3$, or 

usually represented , and indicating that the hydrogen atom at one corner of the hexagon is replaced by a methyl group. Such an alkyl group introduced into the benzene **nucleus** is termed a **side chain.**

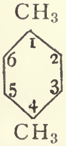
In deriving the formula of the next higher member of the series, xylene, we are met with the fact that three compounds are known to exist, each containing two methyl groups, and this can be best explained by numbering the corners of the hexagon, and introducing the second methyl group into the nucleus in the three possible positions as shown, the compounds being termed the ortho- (*o*-), meta- (*m*-), and para- (*p*-) compounds.



1 . 2 dimethyl benzene
(ortho-xylene or
o-xylene)

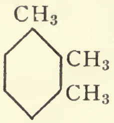


1 . 3 dimethyl benzene
(meta-xylene or
m-xylene)

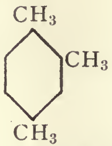


1 . 4 dimethyl benzene
(para-xylene or
p-xylene)

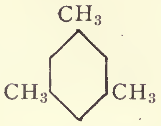
From these three dimethyl benzenes, there are only three trimethyl benzenes possible, *viz.*,



1.2.3 trimethyl benzene



1.2.4 trimethyl benzene



1.3.5 trimethyl benzene

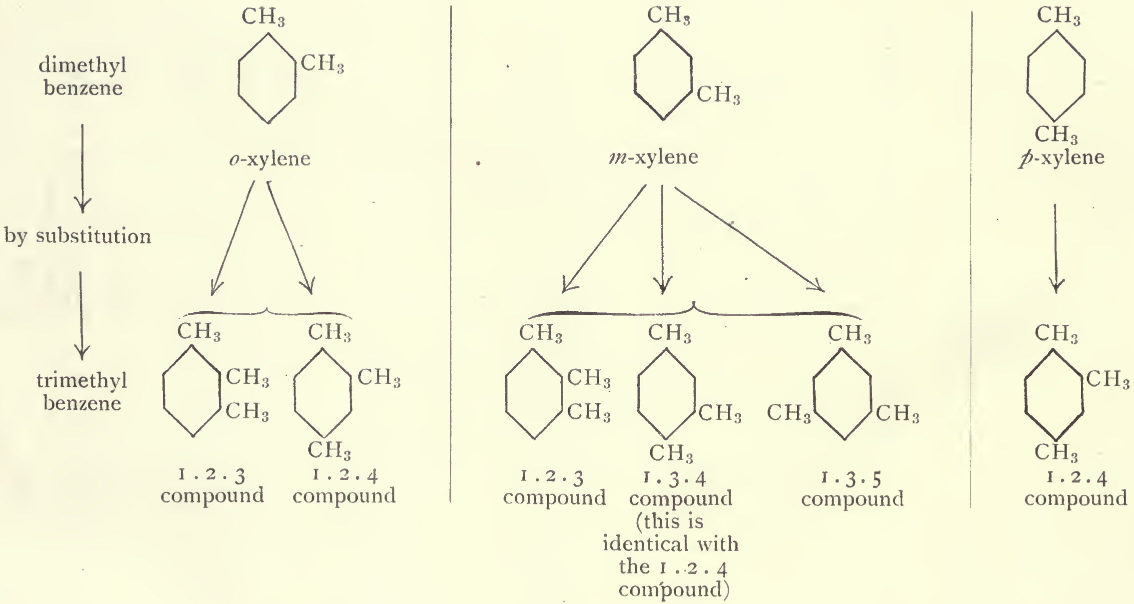
It will be observed that the 1.2.5, 1.3.4, 1.4.5, and 1.4.6 compounds are identical with the 1.2.4 compound; similarly 1.2.6 is identical with 1.2.3.

By starting with the *o*-xylene it is only possible to obtain from it, by this process of substitution, two trimethyl derivatives; with the meta-xylene three dimethyl compounds may be obtained and from the para-compound only one can be got. This is shown in the series of formulae on the following page.

By suitable reactions it is possible from the three xylenes to introduce a third methyl group, and by these reactions we can thus identify the xylenes having the respective structures shown by the ortho-, meta- and para-positions. Thus if one of the xylenes is found experimentally to give rise to two substitution products, the xylene must be the ortho-compound; if three derivatives are obtained it is the meta-compound, but if only one can be prepared it is the para-compound.

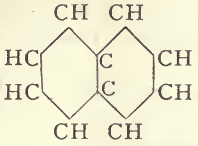
Distillation of coal tar. These hydrocarbons are obtained by fractional distillation of coal tar, obtained in the destructive distillation of coal for the manufacture of coal gas. The tar is distilled and the following fractions are collected:

		B.P.	Yield	Sp. gr.
Coal tar →	Light oil or first runnings	up to 170° C.	2—6 °/o	0·9—0·95
	Middle oil or second runnings	170°—230° C.	10—12 °/o	0·95—1·01
	Heavy oil or creosote oil	230°—280° C.	8—10 °/o	1·01—1·05
	Anthracene oil	280° C. to end of distillation	16—18 °/o	1·05—1·1
	Pitch	left in still	about 50 °/o	—


dimethyl benzene
by substitution
trimethyl benzene
CH_3
CH_3
o-xylene
CH_3
CH_3
CH_3
1 . 2 . 3 compound
CH_3
CH_3
CH_3
1 . 2 . 4 compound
CH_3
CH_3
m-xylene
CH_3
CH_3
CH_3
1 . 2 . 3 compound
CH_3
CH_3
CH_3
1 . 3 . 4 compound (this is identical with the 1 . 2 . 4 compound)
CH_3
CH_3
CH_3
1 . 3 . 5 compound
CH_3
CH_3
p-xylene
CH_3
CH_3
CH_3
1 . 2 . 4 compound

The **light oil** consists principally of benzene, toluene, xylenes, etc.

The **middle oil** contains naphthalene, having the following formula,



phenol and creosols, etc., and is the chief source of these bodies commercially.

The **creosote oil** contains higher phenols, naphthols, etc., and is used for creosoting timber and the waterproofing of felt.

The **anthracene oil** contains anthracene and derivatives, these compounds being crystallised, extracted by various solvents, and re-crystallised.

The **green oil**, remaining after crystallisation of the anthracene and derivatives, is used as a lubricating oil.

Treatment of light oil for the preparation of benzene, solvent naphtha, etc. The light oil is mixed with caustic soda (1·07 sp. gr.), and the upper layer of oil washed with water to remove alkali. It is then treated with sulphuric acid (one part acid, two parts water) and the upper layer again washed with water. The oil is then fractionated, using a fractionating column, such as is shown in Fig. 86, and practically pure benzene, toluene, and commercial xylene are obtained. The portions distilled off above the boiling point of the xylenes furnish **solvent naphtha**, used in waterproofing with rubber.

Properties of benzene. Benzene is a volatile, colourless liquid, boiling at 80·5° C., and insoluble in water, floating on the water owing to its specific gravity being about 0·87. It burns with a very luminous but sooty flame. It is an excellent solvent for organic substances, and is used in the textile industries as a solvent for fats, resins, etc. It is made use of for this purpose as a detergent, particularly in dry cleaning, but must not be confused with "benzine," the commercial product already mentioned, which is a mixture of hydrocarbons obtained in the distillation of petroleum.

Halogen derivatives. Chlorine and bromine act upon benzene forming substitution products, but with toluene and higher compounds the conditions of the action regulate the entrance of the halogen into the benzene nucleus or into the side chain. Thus with chlorine in the cold, and with iron as a catalytic agent, the halogen enters the nucleus, forming three chlor-toluenes, $C_6H_4ClCH_3$, etc., but in the absence of a catalyst and at the boiling point of toluene (or in sunlight) the atom of chlorine enters the side chain, forming benzyl chloride, $C_6H_5CH_2Cl$.

The halogen derivatives may be made use of in the syntheses of Fittig, and Friedel and Craft, for the introduction of alkyl groups or aliphatic side chains into the benzene nucleus, these reactions being similar to the one already described in Chap. XXII for the synthesis of the paraffin hydrocarbons.

Fittig synthesis. A halogen derivative of an aromatic hydrocarbon is treated with an alkyl bromide or iodide and sodium in an ethereal solution:

$$\underset{o\text{-brom-toluene}}{C_6H_4BrCH_3} + CH_3Br + 2Na \rightarrow 2NaBr + \underset{o\text{-xylene}}{C_6H_4(CH_3)_2}$$

Friedel and Craft's synthesis. An aromatic hydrocarbon is treated with an alkyl halide in the presence of anhydrous aluminium chloride as a catalytic agent:

$$C_6H_6 + CH_3Br + AlCl_3 \rightarrow AlCl_3 + HBr + \underset{\text{toluene}}{C_6H_5CH_3}$$

Sulphonic acids. With concentrated sulphuric acid, benzene and its derivatives form sulphonic acids. These are an important group of compounds containing the group of elements $—SO_3H$, and in the case of benzene may be formed by heating with strong sulphuric acid:

$$C_6H_6 + H_2SO_4 \rightarrow \underset{\text{benzene sulphonic acid}}{C_6H_5(SO_3H)} + H_2O$$

Di-sulphonic acids and higher compounds are similarly formed, and are also obtained from toluene and higher derivatives.

Nitro-derivatives. Benzene is a very stable body but is readily attacked by concentrated nitric acid, forming nitro-derivatives, such as nitrobenzene $C_6H_5 \cdot NO_2$, di-nitrobenzene $C_6H_4(NO_2)_2$, etc.

The compounds from benzene and its homologues, formed in this way by the replacement of H by halogens, the nitro- or sulphonic acid groups, form the starting points in the preparation of a great number of compounds which are of importance in the textile industries, particularly the compounds which are known as dyestuffs.

Nitro-benzene, $C_6H_5 \cdot NO_2$. The nitration of aromatic compounds is an important one, and many methods are used, the particular one employed depending on the nature of the compound, whilst the degree of nitration is regulated as a rule by the conditions. Nitric acid, or a mixture of nitric and sulphuric acids, is generally used as the nitrating agent.

In producing nitro-benzene, a mixture of nitric and sulphuric acids is slowly added to benzene in an iron vessel with continual stirring, and the liquid cooled during the action. The liquid is kept at about 40° C., but towards the end may reach 75° C. The lower acid layer is separated, concentrated and used again. The upper layer of nitrobenzene is washed and distilled, either directly or by steam distillation.

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

Nitrobenzene is a yellow oily liquid, boiling at 208° C., and is used on a large scale in the manufacture of aniline. It is known commercially under the name "oil of mirbane" or "artificial oil of bitter almonds."

Aniline, $C_6H_5NH_2$. Nitrobenzene is reduced by means of scrap iron and hydrochloric acid in iron vessels, the liquid being well stirred and distilled in steam. The distillate may be purified by a further steam distillation, the method on a laboratory scale being shown in Fig. 88.

$$C_6H_5NO_2 + 6H \rightarrow C_6H_5NH_2 + 2H_2O$$

It is a colourless liquid, with a boiling point of 184° C. As aniline possesses properties similar to the aliphatic amines it readily forms salts, such as aniline hydrochloride, $C_6H_5NH_2 . HCl$, known as **aniline salt.**

Aniline and its salts are used in the production of **aniline black** in dyeing and printing, and for this purpose should be free from **toluidines,** $C_6H_4CH_3NH_2$ (derived from toluene), the pure aniline oil for this purpose being termed **aniline for blue. Aniline for red** contains ortho- and para-toluidines in addition to aniline, and is used in manufacturing **magenta.**

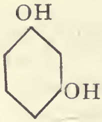
Phenol (carbolic acid), C_6H_5OH. Phenol may be obtained from benzene or aniline, but is usually obtained commercially from the middle oil separated in the distillation of coal tar.

It forms colourless crystals, when pure, melting at 42° C. In the commercial form it is known as carbolic acid, and is used as an antiseptic. The phenols have weak acidic properties, and do not form aldehydes, though they form esters and ethers, consequently they cannot be considered as true alcohols, and must not be confused with the **aromatic alcohols,** in which the alcoholic hydroxyl group is present in the side chain, *e.g.*, **benzyl alcohol,** $C_6H_5 . CH_2OH$.

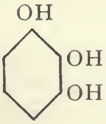
The three **cresols,** $C_6H_4 . OH . CH_3$, which belong to the phenols, are derivatives of toluene and are isomeric with benzyl alcohol; they are used as antiseptics and are made soluble in water by means of resin soap.

Other important compounds of this group are

Resorcinol or **Resorcin,**



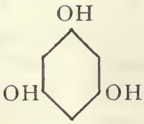
Pyrogallol or **Pyrogallic acid,**

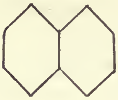
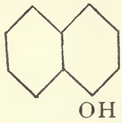
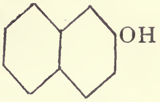


(1.2.3-trihydroxy-benzene)

and

Phloroglucinol,



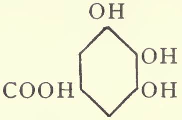
Other hydrocarbons, such as **naphthalene,** , give rise to compounds similar to the phenols, such as α-**naphthol,** , and β-**naphthol,** 

The **aromatic alcohols** give rise to **aldehydes** and **aromatic acids,** which correspond in their respective properties to the similar groups of compounds in the aliphatic series:

$$\underset{\text{Benzyl alcohol}}{C_6H_5 . CH_2OH} \rightarrow \underset{\text{Benzaldehyde}}{C_6H_5 . CHO} \rightarrow \underset{\text{Benzoic acid}}{C_5H_5 . COOH}$$

Salicylic acid, $C_6H_4(OH) . COOH$, which is an important antiseptic, is *o*-hydroxy-benzoic acid, and both this compound and benzaldehyde are used largely in the manufacture of dyestuffs. It is used as an antiseptic dressing for textile materials (see Chap. XXXVIII, p. 341).

Gallic acid (1 . 2 . 3 . 5-trihydroxy-benzoic acid),



is found in small quantity in gall nuts, tea, sumac, etc., and in combination with glucose, termed glucosides, in several tannins. In the glucosides, the hydroxyl groups of the sugar are in combination with the gallic acid forming an ester. The acid is used in the manufacture of inks.

Tannic acid, gallo-tannic acid or **digallic acid,** occurring in gall nuts, sumac, etc., is probably $C_{14}H_{10}O_9$, two molecules of gallic acid condensing with elimination of one molecule of water, though the constitution of the acid is unknown. It is soluble in 6 parts of cold water, and very soluble in hot water. Gelatine is precipitated by tannic acid from solutions of gelatine, glue, etc., the gelatine forming an insoluble body with the tannic acid. This property makes it useful in the treatment of animal skins in the production of leather. It is also largely used in dyeing and printing, and in the manufacture of inks and dyestuffs.

Tannin matters. This term is applied to a large number of vegetable products containing tannic acid, such as myrabolans, cutch, sumac, divi-divi, oak bark, gall nuts, etc. The tannin matter is extracted from these bodies in the form of an aqueous extract. Their use in cotton dyeing is based on the fact that the fibre absorbs the tannin readily, and a basic dyestuff may then be taken up by the fibre. The salts formed by the tannic acid with the colour bases are not fixed, however, on the fibre by this means, but if the tannin treatment is followed by treatment in a solution of a metallic salt, such as an antimony salt, there is formed an insoluble metallic tannate, which adheres firmly to the fibre and readily takes up and fixes basic dyes. An antimony salt, known as **antimony tannate**, is put on the market for this purpose, as a substitute for tartar emetic, antimony oxalate, antimonine, and other similar compounds already dealt with, but the composition of the tannate is doubtful. Tannic acid is also used for loading silk.

PART IV

TECHNICAL CHEMISTRY

(As applied to the Textile Industries)

(Dealing briefly with the chemistry of some of the principal operations in the Textile Industries, and the more important chemical compounds employed in these operations.)

NOTE:—*Many of these compounds have already been fully dealt with in the previous parts, and in some cases the operations have been fairly fully described; in these cases cross-references are given to the earlier portions of the work.*

CHAPTER XXXIII

TEXTILE FIBRES

VEGETABLE FIBRES: COTTON: FLAX: HEMP: JUTE: RAMIE OR CHINA GRASS: ANIMAL FIBRES: WOOL: SILK: MINERAL FIBRES.

The fibres used in the textile industries are divided into the following main classes:

(1) Vegetable, (2) Animal, (3) Artificial, (4) Mineral.

(1) Vegetable fibres.

The chief constituent of vegetable fibres is cellulose (see Chap. XXXI, p. 296); these fibres may be divided into two main branches:

(*a*) Fibres obtained from seed hairs, such as cotton which exudes from the seed capsules of certain species of plants.

(*b*) Fibres obtained from the stalks and bast cells of plants from which the woody fibre has been separated, such as flax, hemp, jute, ramie, etc.

Cotton. The cotton fibre is obtained from a species of plant named *Gossypium*, of which there are a number of varieties, growing to different sizes up to over 20 feet in height, and furnishing fibres which differ in length, fineness and colour. The cotton exudes from the ripe fruit when the seed capsules burst, and the cotton fibre is separated from the seeds by a process termed **ginning**.

The cotton fibre, when examined under the microscope, has the appearance of a flattened tube twisted into a spiral form, with a central tube-like cavity usually present, termed the *lumen*. The fibre is covered by a cuticle or skin, which is rendered more evident by dissolving the cellulose of the cotton in ammoniacal copper oxide, and examining the action under the microscope. The cellulose swells up into a gummy mass, and the cuticle, practically unattacked, appears to be binding the cotton like a piece of string or cord, finally breaking into fragments.

In the raw state, cotton consists of about 90 per cent. cellulose, 8 per cent. of water, and small quantities of fat, wax, etc., the small amount of wax being usually removed during bleaching operations.

As the cotton consists so largely of cellulose, its reactions are very similar to those of cellulose, but it is less hygroscopic. The action of acids and alkalis on cellulose has been already dealt with in Chap. XXXI (p. 297).

Cotton has little attraction for metallic salts, but certain metallic oxides have an affinity for the cotton fibre, and this action is made use of in mordanting processes. Tannic acid has a very strong affinity for cotton, and is used in large quantities for mordanting and fixing purposes in cotton dyeing.

Mercerisation of cotton. The cotton is treated in the cold with a solution of caustic soda, 20 to 25 per cent. in strength, under tension, and the material is washed whilst under tension, thus acquiring a silky lustre, particularly if in the form of yarn from Egyptian or Sea Island cotton. Other substances, *e.g.*, nitric acid, caustic potash, etc., of suitable strengths also bring about a similar effect, but are not used commercially. During mercerisation the flattened fibres become rounder in form, and shrink in length, the contraction being approximately 25 per cent. whilst the strength of the fibres is increased by approximately 12 per cent. Mercerised cotton has a greater affinity for colouring and tannin matters than the unmercerised material, and this test may be used for distinguishing between mercerised and ordinary cotton.

Another method of distinction is to make use of iodine dissolved in potassium iodide and zinc chloride. To prepare the solution 1 to 2 parts of iodine are dissolved in 5 parts of KI and 10 parts of water, and to this is added 25 parts of zinc chloride dissolved in 12 parts of water. The separating iodine is settled and the clear solution used for the test.

The unwetted cotton is immersed in the solution, both ordinary and mercerised material turning blue, but when washed with water without exposure to air, the blue colour remains in the case of mercerised cotton whilst with ordinary cotton the colour is removed.

Flax, Linen. This is obtained from a plant genus named *Linum*, the fibres being obtained from the stems by a fermentation process termed **retting**. The stems are broken up in either stagnant or running water, and the woody matter afterwards broken up and removed by mechanical processes, known as **breaking** and **scutching**, the fibres being finally laid parallel by steel combs in a process known as **heckling**.

The fibres, when examined microscopically, are seen to be in the form of cylindrical tubes, with transverse markings and terminated with conical ends. Flax is composed essentially of cellulose, but the percentage of this substance is less than in cotton. Its reactions are very similar to those of cotton, but dyeing is more difficult, probably due to a difference in physical structure or to compounds not readily removed from the fibre such as pectic matter. Flax is recognised by its cold handle, due to the fact that it conducts heat better than cotton.

Hemp. These fibres are obtained from a plant genus named *Cannabis* by methods similar to those used for the production of flax, and under the microscope the fibres resemble flax in appearance. In addition to pure cellulose the fibres always contain from 25–30 per cent. of lignified matter.

Jute is similar to hemp but of a coarser nature. In distinction from the other vegetable fibres, jute contains no pure cellulose and consists chiefly of lignified matter.

China grass or ramie. This is the bast fibre of a species of nettle cultivated chiefly in China and India ; it is extracted by a process of beating and washing. It possesses a gloss similar to that of silk, superior to that shown by linen, and consists of about 80 per cent. cellulose.

The following reactions will serve to distinguish between flax, hemp and jute.

	Under microscope	With aniline sulphate	With conc. nitric acid	Iodine and sulphuric acid
Flax	fibres have pointed ends	no colour		blue colour
Hemp	thickened rounded ends to fibres, often forked	yellow colour	pale yellow colour	green to dirty yellow colour
Jute	cell walls thickened irregularly	yellow colour	red brown colour	yellow stain

(2) Animal fibres.

The two chief fibres of this class are wool and silk, and these only will be considered.

Wool. Sheep's wool is the principal one of the animal textile fibres and is the hairy covering of the sheep, though the term wool is also applied to the fibres obtained from the hair of goats (**cashmere** and **mohair**), the llama (**alpaca**) and **camel's hair**.

Wool varies considerably in quality, and according to the breed and cultivation of the sheep or goat, and the part of the animal from which it is obtained. The variations in quality are chiefly in lustre, length of the fibres, and degree of fineness, strength, colour, resistance or readiness of the fibre to felting, etc., but the main characteristics are the same in all the different varieties. The wool obtained from living sheep is superior to that obtained from diseased sheep, or those dead from disease, the latter giving lighter and duller shades in dyeing, and does not produce the same handle in finishing processes as wool taken from the living animal.

As it comes into the market in the raw state, wool is very impure, the fibres being coated with fatty or greasy bodies, known as **yolk** or **wool-grease**, amounting on the average to approximately one-third of the weight of the wool itself. The wool-grease contains higher alcohols, cholesterol and isocholesterol, in combination with fatty acids, and may be removed by washing or scouring with soap and dilute sodium carbonate solution, or by extracting with volatile solvents such as benzol, petrol, etc.

In addition, the wool contains potassium compounds of organic acids, known as **suint**, which are also removed in the scouring process. Earthy impurities are also simultaneously removed, whilst **burrs** consisting principally of vegetable matter, or cellulose largely, are later removed by the process of carbonising.

After **scouring**, the wool is put through a **carding** machine, where the fibres are brought more or less parallel to each other, and the material is afterwards **combed** to separate the long-stapled fibres (**tops**) from the short-stapled ones (**noils**). The long-stapled quality is spun into **worsted** yarn, or the shorter staple may be carded and spun into **woollen** yarn. In the English method of **spinning** (ring or cap), about 2 per cent. of oil, generally olive oil, is added to the material. The oil must be removed from goods by scouring operations before the material is dyed. The fibres in worsted yarn lie practically parallel to each other, whereas in woollen yarn the fibres are felted by a subsequent milling process.

When viewed under the microscope, the wool fibre is seen as a thick-walled serrated tube, the outside of which is covered with a large number of serrations or **scales**, enclosing the wool fibre. Within the scaly epidermis is the **cortex** consisting of a great number of spindle-shaped cells showing as striations when examined longitudinally, and within the cortex is a cavity of approximately globular cells. The scaly epidermis plays an important part in the **felting of wool**, as the curliness and elasticity of the wool will cause the protruding edges of the scales of fibres lying in opposite directions to lock together, producing matting of the fibres or felting. Any process which causes the free ends of the scales to protrude to a greater extent will increase the felting property, and the felting process may therefore be accelerated by heat in the presence of water, alkali, acid or certain salts, as in milling or fulling with a solution of soap in water.

Mild alkalis, such as sodium carbonate, and soap are generally sufficient for this purpose, and acid is only used when hard felts are required, as in making felt for hats, etc.

From a chemical point of view, pure wool fibre is a complex substance of the following approximate average composition: C, 50 per cent., H, 7 per cent., O, 22 per cent., N, 17 per cent., S, 4 per cent. It varies, however, in composition very considerably in different specimens, particularly in the amount of sulphur, and the constitution has not been ascertained, though it appears to be amphoteric in character, possessing both acid and basic groups, dissolving in caustic soda and combining readily with basic dyestuffs, whilst it also absorbs acids which cannot be totally eliminated by washing.

Sulphur may be detected in wool by heating with sodium plumbite (lead monoxide dissolved in caustic soda), when black lead sulphide is formed.

The presence of nitrogen is shown by burning wool, when an odour of ammonia is observed, and if the wool is heated in a test tube the presence of ammonia may be detected by red litmus paper. A portion of the nitrogen is present as amido-nitrogen, as the material may be diazotised with nitrous acid in a manner similar to aniline.

Action of water, acids, and alkalis on wool.

Action of water. Water has little action on wool, unless boiled with it for a prolonged period when slight action occurs, but steam has a pronounced action, particularly if the steaming is prolonged, the action being more marked than in the case of cotton.

Mildew is liable to be produced by the action of water at a moderate temperature, the fibre being affected so that the affinity for dyestuffs is considerably diminished.

Action of acids. **Strong sulphuric acid** dissolves wool, and dilute acid has a marked action, though solutions containing 5 or 6 per cent. of sulphuric acid have little action. In the cold, or on boiling with this dilute acid, some of the latter is absorbed, a portion being removed by subsequent washing, though a certain amount is retained by the wool. Dilute sulphuric acid is used in dyeing wool in an acid bath.

Hydrochloric acid behaves in a similar manner to sulphuric acid.

Nitric acid stains wool a yellow colour, probably due to the production of xantho-proteic acid. The action has been made use of in "stripping off" the colour from dyed woollen materials previous to re-dyeing. The action of concentrated nitric acid is also employed for producing false selvedges of a yellow colour on woollen materials.

Organic acids have practically no action on wool, but are absorbed in a manner similar to the absorption of inorganic acids, with the production of salts or addition compounds.

Action of alkalis. The action of **caustic alkali** is much more drastic in the case of wool than cotton, and a 1 per cent. solution of caustic soda will dissolve wool on boiling for some time.

In a **strong caustic soda** solution, the properties of wool are affected in a manner somewhat similar to the mercerising of cotton, though shrinkage of the material is absent. Use is made of this property in the production of **crape** by passing goods containing both wool and cotton through strong caustic soda solution, the cotton being shrunk whilst the wool gives rise to the crape effect; the alkali is then removed by "souring" with dilute acid.

The action of **alkali carbonates** is much less than that of caustic alkalis, though they have a destructive action on wool if strong hot solutions are used. For milling and scouring they are used in conjunction with soap at a moderate temperature, but affect the condition and handle of the wool.

Ammonia has very little action on wool.

It should, however, be noted that the lustre of wool may be destroyed by prolonged treatment with practically all substances, and even most neutral salts have a decided action by boiling in solution with wool for considerable periods. This action is probably due to the amphoteric nature of the wool, the neutral salt being probably decomposed with the formation of wool-acid and wool-alkali products. The mordanting of wool with certain metallic salts, such as sulphate and chloride of aluminium, tin, etc., depends upon a similar action.

When treated with **hypochlorite solutions**, similar to those employed in bleaching cotton, wool is darkened in colour, its affinity for dyestuffs is increased and its felting properties reduced. This action is made use of in the production of **unshrinkable wool**, and the action is also important in the printing of **delaines** or **union goods** of cotton and wool, so as to cause the printed colours to penetrate and be absorbed by both fibres equally.

Silk. Silk, although of animal origin, is very different from wool. The fibre is the secretion of the larvae of certain moths, and is exuded by the animal in passing from the larva to the pupa stage. The solidified silk fibre is wound round its body in a continuous and regular manner, the length varying from $\frac{1}{4}$ to 2 miles, and in about four days the cocoon is completed. The pupae in the cocoons are killed by heating or steaming, and are then steeped in hot water to soften the surrounding gum, when the silk fibre can be drawn off by a process known as **reeling**.

The raw silk obtained by reeling consists of the silk fibre (**fibroin**) surrounded by a layer of gum (**sericin**), the latter being removed by boiling, and constituting about 25 per cent. of the raw silk. The fibroin corresponds to the formula, $C_{15}H_{23}N_5O_6$, and the sericin, $C_{15}H_{25}N_5O_8$. Under the microscope silk has the appearance of a rod-shaped fibre. It is extremely hygroscopic and may take up 30 per cent. moisture without appearing to be wet.

Silk is affected by long boiling with water, and under pressure may be dissolved by the water. It is not affected by heating to 100°C., but at 160°C. a fairly rapid decomposition takes place, becoming first brown and then black. When burnt in the air it behaves similarly to wool.

Action of acids, alkalis, etc., on silk.

Silk is soluble in **concentrated acids**, but when treated with dilute acids it retains a portion, the lustre being increased, whilst the material acquires the peculiar property of the **scroop of silk**, a name given to the crackling sound emitted when squeezed in the hand. Dilute and concentrated nitric acid give a yellow colour to the silk.

At low temperatures, **caustic alkalis** have little effect, but at higher temperatures dissolve silk, though not so easily as in the case of wool.

Metallic salts are readily absorbed, and bodies such as stannic chloride are used in the mordanting and weighting of silk.

A strong solution of zinc chloride, or an ammoniacal solution of nickel hydroxide will dissolve silk, and this action may be made use of for the separation of cotton and silk.

Wild silk. There are several varieties of wild silk, produced by certain varieties of the wild silk-worm, but the most important is Tussar or Tussah silk. As placed on the market it has a brown colour, which is not easily removed. Caustic soda has only a very slow action upon it, and in this respect it differs from cultivated silk, whilst it is also a harder fibre, thicker, and dyes with greater difficulty than cultivated silk.

(3) Artificial fibres.

These are dealt with in detail in the next chapter, see p. 318.

(4) Mineral fibres.

These, from the point of view of use in textile industries, are of little importance. The principal ones, which may also in some cases be considered as artificial fibres, are **metallic threads**, consisting of a very fine wire such as copper, silver and gold ; **spun glass**, consisting of glass, which may be coloured, drawn out when hot into continuous fine threads ; and **asbestos fibres**, which are produced from the naturally-occurring fibrous mineral asbestos. The latter consists of a silicate of iron and magnesium, and may be spun into yarn and woven into cloth, or made into hard boards. As it is not affected by heat, it finds a useful application in the production of **fire-proof materials.** It is also unaffected by acids or alkalis, and this substance and also glass wool are largely used for chemical purposes as a filtering medium.

Slag wool is a similar product, which is produced by blowing steam through molten slag. It is a good non-conductor of heat, and is used as a packing material in glands and for **lagging steam pipes.**

CHAPTER XXXIV

ARTIFICIAL FIBRES

ARTIFICIAL SILK: CHARDONNET SILK: PAULY SILK: VISCOSE SILK: PROPERTIES OF ARTIFICIAL SILK.

Artificial fibres, like those of natural origin, may be divided into several classes according to their origin. Thus certain fibres, mentioned in the last chapter as of mineral origin, may be looked upon as artificial fibres, namely, metallic, glass, and asbestos fibres and slag wool, but in this chapter it is only proposed to deal with those of vegetable origin, which in recent years have become of great importance in textile industries. This class consists principally of artificial silk produced from cellulose or from wood pulp.

Artificial silk.

As the silk fibre, consisting of the solidified secretion exuded by the silk-worm, is devoid of cellular structure, it obviously offers better prospects of artificial production than the other natural fibres. Various processes have been devised for its production which depend upon the solution of cellulose or its derivatives in suitable reagents, the viscous liquid being afterwards forced by pressure through minute orifices into liquids in which it solidifies, and fibres are produced which in lustre are practically indistinguishable from the best natural silk.

Chardonnet silk from nitro-cellulose. Count de Chardonnet has worked out a successful process for the production of artificial silk from cellulose, which in broad outline is as follows.

Wood pulp, after disintegration and drying at 150° C., is treated with a mixture of nitric and sulphuric acids. The acid is drawn off, and the material freed from excess in a centrifugal extractor, finally washed well in water and dried at a low temperature. The nitrocellulose produced is then dissolved in a mixture of equal parts of alcohol and ether to form a 20 per cent. solution, thus forming the liquid "collodion," already described in Chap. XXXI (see p. 297). The liquid is filtered, and forced through fine orifices, where the material immediately encounters a fine jet of water, and the thread obtained is led into a trough of water. Several of these extremely fine threads are drawn together, and given a slight twist in order to increase the lustre. The alcohol dissolves in the water, and the ether vapour is drawn off and condensed for further use.

The fibres, after reeling, are de-nitrated by immersion in a slightly warm solution of ammonium sulphide, in order to render the material less inflammable, and the artificial silk is then well washed and dried.

Pauly's process. In this process the cellulose is dissolved in the cuprammonium solution known as Schweitzer's reagent, described in Chap. XXXI (see p. 296), until sufficiently viscous. The liquid is forced through fine orifices into a dilute acid, such as sulphuric or acetic acid, the fibre is well washed, and reeled. It is known under the names **cuprammonium silk, Pauly silk** and **glanzstoff.**

A strong solution of zinc chloride has also been used for the solution of cellulose in the production of artificial silk.

Viscose silk. In this process, cotton is mercerised and then treated with carbon disulphide to produce Cross and Bevan's cellulose xanthate. This substance when dissolved in water is very viscous, and has been termed **viscose.** It may be converted into artificial fibres by a method similar to that employed with the cuprammonium solution, the xanthate decomposing on drying and producing a very lustrous thread, known as viscose silk.

Properties of artificial silk. Although artificial silk can be made as soft as the natural product, and with as great or even greater brilliancy and gloss, yet it only possesses about two-thirds the tensile strength of the natural product and its covering power is less. It also becomes weaker still when wetted, whereas cotton and linen, which are also cellulose, become stronger in the wet condition. The artificial product, however, regains its strength on drying. The general properties are those of cellulose, but the different products vary slightly in properties, thus Chardonnet silk still contains nitric acid and some sulphur, and exhibits an attraction, unlike cotton, for basic dyes.

The capillary tubes from which the fibres are formed are about 0·0025″ in diameter, and since the fibres contract considerably on drying, they are only about 0·001″ in diameter, though this is not as fine as the natural silk fibre. A double skein of artificial silk weighing from 15 to 20 grams will have a length of about 1000 metres, and since each thread will contain as a rule about 15 filaments, an ounce skein will contain approximately 30,000 yards of fibre, or one pound over 250 miles of fibre.

CHAPTER XXXV

SCOURING AGENTS AND DETERGENTS

SOAP AS A SCOURING AGENT: ANALYSIS OF SOAP: TEXTILE SOAPS: VEGETABLE SOAPS: AMMONIUM HYDROXIDE, AMMONIUM SALTS, AND ALKALI CARBONATES AS SCOURING AGENTS: VOLATILE LIQUIDS FOR SCOURING: DETERGENTS: CHLOR DERIVATIVES OF ETHANE AND ETHYLENE: BENZINE SOAPS: SOAP EMULSIONS: TETRAPOL: REMOVAL OF IRON AND INK STAINS.

The term scouring agent is usually applied to materials which are used in washing, *e.g.*, in the scouring or washing of wool, and the principal agent employed is soap or its varieties, frequently used in conjunction with other bodies such as weak alkalis. The term detergent is employed here to indicate the general class of bodies which are used as cleansing materials, so that it includes the substances used to remove stains as well as those employed in the removal of dirt or grease.

In order to employ these bodies to the best advantage, it is necessary not only to have a knowledge of their composition, but also to know their action on the various textile fibres and the material giving rise to the stain. A stain due to iron cannot, for example, be removed by a body which forms an insoluble substance with the iron, as in order to remove the metal, a soluble body must be produced, and this illustration may be applied more or less generally to the use of scouring agents and detergents.

Scouring agents.

Soap. The choice of a soap depends largely on the process for which it is required, *e.g.*, in the scouring of wool, a small amount of free alkali, particularly caustic alkali, is objectionable owing to the deleterious action on the fibre. If, however, the wool has received an acid treatment, it may be an advantage to wash it afterwards with soap containing a small quantity of alkali, so as to neutralise the trace of acid retained by the wool.

Soda has a more deleterious effect on wool than potash, so that potash or soft soaps are preferable for wool washing, though a neutral hard or soda soap is preferable even to a potash soap which contains free or uncombined alkali. As a rule, on account of cheapness, hard soaps are commonly employed in wool scouring, but for the best qualities of wool it is preferable to use potash or soft soaps made from Gallipoli or olive oil.

Ammonium chloride is occasionally used in wool scouring to remove the trace of free alkali, the liberated ammonia assisting in the scouring operation without acting on the wool.

The main action of the soap in cleansing wool is to form an emulsion with the suint or yolk, and thus remove it together with the adherent mineral matter. Sodium carbonate assists the emulsifying power of the soap and aids the removal of the grease, but its use must be carefully controlled, as if the solution is too strong or the temperature too high (about 35° C. is the best) the wool may suffer considerably. For this purpose the sodium carbonate must be free from caustic alkali, and it should be tested for free caustic by the method detailed in Chapter XII (p. 104).

Soaps containing borax and sodium silicate are sometimes used as detergents, but are best avoided in textile work, particularly in wool washing.

Analysis of soap. For a complete analysis of soap, suitable works on analytical chemistry should be consulted, as only a brief description of the methods of valuing a soap by the estimation of (1) water, (2) fatty anhydrides, (3) total alkali, and (4) combined alkali, will be given.

Sampling. In the case of a hard soap, the portions for analysis should be cut from the middle of the bar, and with a soft soap from a portion under the surface.

(1) **Estimation of water.** About 5 grams of the soap in thin shavings are weighed in a shallow porcelain dish, and heated in an air oven to 110° C. until constant in weight. From the loss in weight, the percentage loss of water may be calculated. With a soft soap, a short glass rod should be used to stir the soap and must be weighed with the dish. Several hours are required in order to obtain a constant weight.

(2) **Fatty anhydrides.** 3 grams of soap are weighed in a small wide-necked flask, a small quantity of water is added, and heated until the soap is dissolved. A few drops of methyl orange solution are added, and N/1 sulphuric acid run in until the solution has a decided red colour. When cool, about 50 c.c. of ether are added to dissolve the liberated fatty acids, and the whole poured into a stoppered or separating funnel. The flask is washed with a small quantity of ether, and the washings added to the bulk in the funnel, which is shaken up and allowed to stand. The lower layer is run off, and the remaining ethereal solution is washed with about 30 c.c. of water which is also tapped off when the layers have separated. The ether extract is then transferred to a weighed wide-necked flask, the funnel rinsed with ether, and the ether distilled off from

the extract and rinsings. The last traces of ether and moisture are removed from the fatty acids by heating in an air oven. The weight of fatty acids may thus be obtained, and multiplied by 0·97 will give the fatty anhydrides, so that the percentage may be calculated.

(3) **Total alkali.** 3—5 grams of the soap are weighed out into a small wide-necked flask and dissolved in water. A few drops of methyl orange solution are added and N/5 sulphuric acid is then run in from a burette until the solution just turns pink.

1 c.c. of N/5 H_2SO_4—0·0062 gram Na_2O.
1 c.c. of N/5 H_2SO_4—0·0094 gram K_2O.

From the number of c.c.'s of N/5 sulphuric acid used, the amount of alkali can be obtained by multiplying by one of the above factors and the percentage calculated.

(4) **Combined alkali.** Dissolve the mixed fatty acids (see estimation of fatty anhydrides) in warm alcohol, add a few drops of phenol phthalein and then titrate to a permanent red tint with N/2 alcoholic KOH. Calculate to Na_2O for hard soaps, and to K_2O for soft soaps.

Uncombined alkali is found by difference. Lewkowitsch gives in *Chem. Tech. of Oils, Fats and Waxes* (Vol. III, pages 310, 335), the following as theoretical compositions of genuine hard and soft soaps, containing fatty acids having a mean molecular weight of 275, but the fatty anhydrides and combined alkali are generally greater than these figures; some typical analyses are given for comparison.

	Theoretical		Actual analyses	
	Hard	Soft	Hard	Soft
Fatty anhydrides	61·60 °/₀	38·70 °/₀	64—72 °/₀	38·4—47·5 °/₀
Combined alkali	7·18	6·84	7—8·5	7·3—10·1
Water, glycerol, etc.	31·22	54·46	19—30	54·3—42·4

The variation is due to the different oils and fats employed in the manufacture of the soap, and it is generally necessary in a complete analysis to get an idea of the nature and quality of the fatty acids, which may be done by determinations of the specific gravity, melting and solidifying points, saponification equivalent or molecular weight of the fatty acids.

Textile soaps. For textile work the quality of the soap required depends on the use to which it is to be put. For **degumming silk**, olive oil soda soaps free from uncombined alkali are much used, though silk manufacturers frequently add a little potassium carbonate or borax to the soap solution.

For raw wool and **yarn scouring**, free alkali, unsaponifiable matter, resin and silicate of soda, should be absent, and cotton seed oil should not have been used for the production of the soap. Potash soap is the best, but soda soaps are commonly employed, and some firms use ammonia soaps.

For scouring low class goods, mungo and **shoddy**, a strongly alkaline soap may be employed, but silicate and resin should be absent.

In the **cotton industry** soaps made from olive or palm oil are employed, but they should not contain free alkali.

Vegetable soaps, such as **Quillaya bark, soap bark, soap root**, etc., are often used as detergents. They contain a glucoside, saponin, $C_{32}H_{52}O_{17}$, which is easily soluble in water, and is broken up by hydrolysis into sapogenin ($C_{14}H_{22}O_2$) and sugar. The former has detergent properties in acid, neutral or alkaline solution, and is useful where an acid material has to be scoured. It is employed in cleaning silks, gloves, and in conjunction with fuller's earth for cleansing woollen materials dyed with indigo.

Ammonium hydroxide, ammonium carbonate, and, as already mentioned, other **alkaline carbonates, such as sodium and potassium**, are used as scouring agents. The amount employed, in the case of sodium and potassium carbonates, depends on the quality of the wool, and where potash soaps are used, it is preferable to employ potassium carbonate, as the use of sodium carbonate causes a double decomposition with the potash soap forming a sodium soap.

Volatile liquids such as **carbon disulphide, CS_2**, and **petroleum spirit** have been suggested for use in wool washing, the material being circulated on the counter-current principle, and the solvent and grease recovered by distillation. Water must be used in conjunction with the volatile solvent for removal of the suint, otherwise the decomposition of the suint occurring later gives a harsh handle to the wool. The process is in successful operation on the continent.

Detergents.

The bodies used as detergents are principally organic substances, **such as alcohol, ether, paraffin compounds, such as petroleum spirit** and **petrol, chloroform, carbon tetrachloride, tetrachloro-ethane, benzine, benzene, etc.** The use of most of these bodies has been described in Part III of this work, and reference should be made to the individual substances for their properties.

These bodies have a good solvent action on oils, fats, tar, pitch, wax, resins, shellac, etc.; and the chlor derivatives, carbon tetrachloride and tetrachloro-ethane, etc., described in Chapters XXIII and XXIX (pp. 247, 248, 284, 285) are particularly useful as they are non-inflammable, and the risks of fire are less with their use.

In removing a grease or oil stain from a fabric by the use of one of these solvents, such as petrol or benzene, the solvent should first be applied round the spot with a clean rag or cotton wool, working gradually towards the stain, in order to prevent the grease spreading into the fabric.

Estimation of oil or grease in yarn or a fabric. This is carried out by extraction with ether, as described in Chapter XXIV (p. 256).

Benzine soaps have been prepared by dissolving an acid salt (alkali oleate) in benzine (about 30 per cent. hydrocarbon), carbon tetrachloride, etc., and these bodies form a milky liquid or emulsion with water, which gives a strong lather on shaking. The soaps combine the powerful cleansing action of ordinary soap with the detergent quality of the solvent. They are largely used in dry cleaning processes, and for the removal of stains from textile fabrics.

Cereal soaps—Sapon soap. Cereals, such as ground maize, wheat, etc., are treated with a definite quantity of caustic soda and water in the cold, and the mixture kneaded into a dough-like mass, possibly containing amino-acids of high molecular weight. It is afterwards converted into a granular powder as **sapon soap meal**, or is made into a soft or bar soap form. The soap is neutral, soluble in water, and insoluble in alcohol; it has no action on the salts present in hard water, and does not form the objectionable lime or magnesia soaps. It is an excellent emulsifier, and by the action of the "surface-active" colloids, which are present, forms a good detergent. No lather is formed in water, but it is also mixed with soap, or the soap may be produced during the process of manufacture, to form a lather, though this is not necessary for its use as a detergent.

Soap emulsions are also produced by neutralising turkey red oil by means of a caustic alkali. The chloro-ethylenes are used in the preparation of these emulsions by dissolving soap in the solvent, and similarly carbon tetrachloride has been emulsified by saponin in the preparation of these bodies. The use of these organic halogen derivatives as detergents, either alone or with certain soaps in solution, depends not only on their solvent action, but very largely on their emulsifying power, and they are being largely employed in detergents of the "tetrapol" class. **Tetrapol**, with an alkaline reaction, is another of these preparations, and when mixed with water behaves like a soap solution. Other similar trade preparations are **Novol**, **Hexol**, etc.

Removal of iron or ink stains. The removal of metallic stains from textile fabrics is of great importance, and substances used in removing them may be also classed as detergents. The removal of iron stains (iron mould) from fabrics is accomplished by dissolving the iron in a solution of oxalic acid or its alkali salts, and even better results are obtained by using it in conjunction with acetic acid. Ink stains, containing iron, can usually be removed by similar treatment.

CHAPTER XXXVI

BLEACHING, DISCHARGING AND MERCERISING AGENTS

BLEACHING AGENTS: CHLORINE: BLEACHING POWDER: SODIUM HYPOCHLORITE AND ELECTRIC BLEACHING: VALUATION OF BLEACHING POWDER: HYDROGEN AND SODIUM PEROXIDES: POTASSIUM PERMANGANATE: OZONE: SULPHUR DIOXIDE AND SULPHUROUS ACID: SODIUM BISULPHITE AND HYDROSULPHITE: DISCHARGING AGENTS: SODIUM HYDROSULPHITE AND FORMALDEHYDE COMPOUNDS: MERCERISING AGENTS: CAUSTIC ALKALIS.

Bleaching agents.

Practically all fibres of vegetable and animal origin are more or less coloured in the natural state, and the process by which these colouring matters are removed or decomposed in order to render the fibres colourless is known as bleaching.

Probably the oldest method of bleaching fabrics is to expose them to the air, by spreading on grass or frames, where they are bleached by the small quantities of hydrogen peroxide and ozone usually present in the atmosphere.

Modern bleaching, however, is purely a chemical process, the chief substances used being: chlorine, Cl; bleaching powder (chloride of lime), $CaOCl_2+Ca(OH)_2$; sodium hypochlorite, $NaOCl$; sodium perborate, $NaBO_3$, $4H_2O$; hydrogen peroxide, H_2O_2; sodium peroxide, Na_2O_2; potassium permanganate, $KMnO_4$; ozone, O_3; sulphur dioxide, SO_2; sodium bisulphite, $NaHSO_3$; sodium hydrosulphite, $Na_2S_2O_4$.

These substances may be divided into oxidising agents and reducing agents, the former including the chlorine compounds and substances which yield oxygen, and the latter the sulphur compounds.

Oxidising agents.

Chlorine, bleaching powder, sodium hypochlorite and electric bleaching. These agents are used only for bleaching vegetable fibres, and cannot be used for wool and silk, since they have a destructive action on these fibres.

The preparation and use of these bodies has already been dealt with in the chapter on chlorine, see Chapter XVIII, p. 174. Chlorine is seldom if ever used in the gaseous state, and it is usually prepared in solution as required. Bleaching powder and sodium hypochlorite furnish a ready method for obtaining these solutions, since they generate chlorine on treatment with dilute acids, and sodium hypochlorite is now largely prepared electrolytically for electric bleaching as described in Chapter XVIII, p. 177.

Valuation of bleaching powder. The valuation of bleaching powder may be carried out in the following manner. About 10 grams are accurately weighed and made into a smooth paste by rubbing with water in a mortar. The paste is washed into a litre flask with water and made up to 1000 c.c. After thoroughly shaking, 25 c.c. is taken out with a pipette and run into a conical flask, 1 gram approximately of potassium iodide being added. The solution is then acidified with dilute acetic acid, and the liberated iodine is titrated with N/10 sodium thiosulphate solution (24·8 grams of $Na_2S_2O_3$, $5H_2O$ dissolved in 1 litre of water), until the solution is almost colourless. A few drops of a starch paste solution are then added to form the blue iodide of starch with the trace of remaining iodine, and the titration continued until the liquid is colourless.

The reactions taking place are:

$$Cl_2 + 2KI \rightarrow 2KCl + I_2$$
$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

Example:

10 grams of bleaching powder taken, in 1000 c.c. H_2O.
25 c.c. of bleaching powder solution required 24·3 c.c. N/10 thio.
1 c.c. N/10 thio. = 1 c.c. N/10 I or Cl = 0·00355 gram Cl.
25 c.c. of solution contain $24·3 \times 0·00355$ gram of Cl.
1000 c.c. of solution contain $24·3 \times 0·00355 \times 40$ grams of Cl.

$$\text{Percentage of available Cl} = \frac{24·3 \times 0·00355 \times 40 \times 100}{10}$$
$$= 34·5 \text{ per cent. available chlorine.}$$

Sodium hypochlorite or electric bleaching liquor. This has already been described in Chapter XVIII, p. 177. It is known also under the names of **Eau de Javelle, Chlorozone, bleaching soda,** etc. The liquor has the advantage of being clean, and being free from lime requires no settling. It contains both sodium hypochlorite and sodium chloride in solution, and when treated with dilute sulphuric acid reacts thus:

$$NaClO + NaCl + H_2SO_4 \rightarrow Na_2SO_4 + Cl_2 + H_2O$$

In the absence of acid it is the available oxygen which brings about the bleaching action, thus:

$$NaClO \rightarrow NaCl + O$$

The valuation of this substance is carried out in a manner similar to that used for bleaching powder.

Hydrogen peroxide. This substance is used for the bleaching of wool, silk, feathers, straw, leather, ivory, horn, bones and hair, and is also sometimes used for the finer qualities of cotton and linen. Its preparation and use have already been described in Chapter XV, p. 132.

Valuation of hydrogen peroxide. The commercial hydrogen peroxide is usually 10 to 12 volumes in strength, and the actual strength may be determined by titration with a N/10 solution of potassium permanganate (3·16 grams of $KMnO_4$ in 1 litre) until a permanent pink colour is obtained. Sulphuric acid must be present in the liquid.

$$\begin{array}{ll} 5H_2O_2+2KMnO_4+3H_2SO_4 \rightarrow & 5O_2+8H_2O+K_2SO_4+2MnSO_4 \\ \qquad\quad | & \quad(\text{Half O from } H_2O_2=5O) \\ \qquad\quad | & \qquad\qquad\qquad\quad | \\ \qquad 316 & \qquad\qquad\qquad\quad 80 \\ \qquad 3{\cdot}16\text{ grams} & \qquad\qquad\qquad\quad 0{\cdot}8\text{ gram}=560\text{ c.c.} \end{array}$$

$\therefore$ 1 c.c. N/10 $KMnO_4$ = 0·0017 gram H_2O_2 = 0·0008 gram O = 0·56 c.c. O.

Example:

2 c.c. of 12 volumes H_2O_2 diluted with water and 5 to 10 c.c. of dilute H_2SO_4 added.

45 c.c. of N/10 perman. used.
Volume of available O in H_2O_2 = (45 × 0·56) c.c.
2 c.c. of H_2O_2 = 25·2 c.c. O.
1 c.c. of H_2O_2 = 12·6 c.c. O = 12·6 volumes strength.

Sodium peroxide, Na_2O_2. This substance can be used for the bleaching of wool, silk, linen, cotton, straw, feathers and hair, though its use is limited to goods of better quality owing to its price. Sodium peroxide is a pale yellow powder obtained by heating sodium at 300° C. in a current of pure dry air. It absorbs moisture and carbon dioxide on exposure to air, at the same time decomposing with liberation of oxygen. It is an extremely powerful oxidising agent, yielding about 20 per cent. available oxygen, so that it is much stronger than hydrogen peroxide in available oxygen. It reacts with iced water to form sodium hydroxide and hydrogen peroxide, thus:

$$Na_2O_2+2H_2O \rightarrow 2NaOH+H_2O_2$$

If the temperature is allowed to rise, oxygen is liberated and sodium hydroxide and water are formed.

$$Na_2O_2+2H_2O \rightarrow 2NaOH+H_2O+O$$

Similar reactions take place with dilute acids, the sodium salts of the acid being formed instead of sodium hydroxide:

Low temperature: $Na_2O_2+H_2SO_4 \rightarrow Na_2SO_4+H_2O_2$
High ,, $Na_2O_2+H_2SO_4 \rightarrow Na_2SO_4+H_2O+O$

In dissolving sodium peroxide, therefore, the water must be as cold as possible, and since a considerable amount of heat is generated during the action, the peroxide must be dissolved slowly. The best method is to sprinkle the peroxide on to a large volume of dilute acid until the solution is nearly neutral, the liquid being continuously stirred. For bleaching purposes it is advisable to remove the last traces of acid with ammonium hydroxide, the presence of free caustic alkali, such as sodium hydroxide, being avoided as it has a detrimental effect on the fibres.

Potassium silicate is also recommended for neutralising the last traces of acid, and the bath is maintained slightly alkaline to red litmus paper during the process by the necessary addition of potassium silicate. The following bath is recommended: water, 100 parts by weight; H_2SO_4, 0·675 parts; 0·5 parts of Na_2O_2 sprinkled into the liquid. Render slightly alkaline with potassium silicate, or a bath twice this strength may be used for bleaching 20 parts by weight of wool.

The wool or silk is first freed completely from impurities by a soap bath containing a little ammonia or sodium carbonate, then washed with water, and steeped in the slightly alkaline bleaching bath for three to five hours. The material is thoroughly washed with water, and finally with very dilute sulphuric acid or acetic acid. In its bleaching action, sodium peroxide is an oxidising agent and the bleach is permanent.

Valuation of sodium peroxide. This is carried out as with hydrogen peroxide, about 0·2 gram of substance being weighed out in a weighing bottle and quickly immersed in about 500 c.c. of water in a dish; sulphuric acid is added and the liquid titrated with N/10 permanganate.

Sodium perborate, $NaBO_3$, $4H_2O$. Several perborates have been described, but the product put on the market may be prepared by the action of hydrogen peroxide and sodium peroxide on boric acid. Hydrogen peroxide is liberated by dilute acids, whilst concentrated sulphuric acid decomposes it, liberating ozone. The hydrogen peroxide liberated by dilute acids may be used as a bleaching agent.

Sapozon is a soap containing perborate which acts as a bleaching agent and a disinfectant, through liberation of oxygen.

Potassium permanganate, $KMnO_4$. This is used for bleaching both animal and vegetable fibres, particularly jute, and may be used for wool, skins, straw, and ivory.

Preparation. It may be prepared by fusing pyrolusite, MnO_2, the common mineral containing manganese, with an alkali in the presence of an oxidising agent or air. Potassium manganate, K_2MnO_4, is formed, but, on boiling with water, the purple permanganate, $KMnO_4$, is produced in solution with precipitation of manganese dioxide. The permanganate is crystallised from the solution.

$$MnO_2 + K_2CO_3 + O \rightarrow K_2MnO_4 + CO_2$$
$$3K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + 4KOH + MnO_2$$

Properties. Potassium permanganate forms purple crystals, easily soluble in 15 or 16 parts of water, giving a purplish-red solution. It acts as a powerful oxidising agent in either acid, alkaline or neutral solution, and is used largely as a disinfectant. In most of its oxidising actions in acid solutions, it yields oxygen according to the equation below and this is termed available oxygen.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 5O + 3H_2O$$

Condy's fluid is a preparation very similar to potassium permanganate, and is said to contain the sodium compound.

Potassium permanganate as a bleaching agent. The permanganate acts as a bleaching agent owing to its powerful oxidising properties. During the process the permanganate is reduced to caustic potash and the brown oxide of manganese, MnO_2, H_2O, is deposited on the fibre. This stains the fibres brown, but the original colour has been destroyed, and the brown stain can be readily removed by subsequent treatment with sodium bisulphite or sulphurous acid solution. The following equations represent the reactions taking place:

$$2KMnO_4 + 3H_2O \rightarrow 2(MnO_2, H_2O) + 2KOH + \underset{\substack{\text{oxygen available} \\ \text{for bleaching}}}{3O},$$

$$2(MnO_2, H_2O) + 4NaHSO_3 \rightarrow 2MnSO_4 + 4H_2O + 2Na_2SO_3$$

When animal fibres are being treated, the caustic potash liberated during the first reaction must be removed or it will damage the fibres. This can be done either by the addition of dilute acid, or by the addition of magnesium sulphate and formation of harmless magnesium hydroxide.

$$2KOH + MgSO_4 \rightarrow Mg(OH)_2 + K_2SO_4$$

The wool is placed in a 2½ per cent. permanganate solution, with magnesium sulphate added, for about one hour, or a stronger solution (5 per cent.) may be used with other materials such as jute, the excess of liquor squeezed off, and then treated with the bisulphite solution acidified with a small quantity of acid. When the brown stain has disappeared, the material is washed and dried.

The bleach is permanent and although expensive is very useful for the treatment of delicate fabrics.

Ozone. The use of ozone as a bleaching agent is chiefly to replace the grass bleaching of linen.

The preparation of ozone has already been described (Chapter XV, p. 137). The fibres are exposed to the action of the ozonised air for several hours, the material being in a slightly moist condition. The results are equal to those obtained in grass bleaching, and the time taken is much less.

Reducing agents.

Sulphur dioxide, sulphurous acid, sodium bisulphite. These have already been described fully in Chapter XIX, p. 182. They are used principally in the bleaching of wool, straw, silk, hemp and leather.

The colourless reduction products formed are gradually oxidised back to coloured substances on exposure to air, and wool which has been bleached with sulphur dioxide gradually resumes its yellowish tint.

Valuation of sodium bisulphite solution. The valuation of sodium bisulphite solutions is usually carried out in the following manner. About 1 gram of the liquid is weighed in a small tube, and the tube and contents are then dropped into a stoppered bottle containing 100 c.c. of N/10 iodine solution (12·7 grams of pure iodine and 35 grams of KI dissolved in 1 litre of water). The stopper is replaced and the bottle shaken. The excess of iodine is then estimated by titration with N/10 sodium thiosulphate and starch solution. The difference between the amount of N/10 thio. required and the 100 c.c. of N/10 iodine taken gives the volume of iodine consumed by the $NaHSO_3$, thus:

$$NaHSO_3 + I_2 + H_2O \rightarrow 2HI + NaHSO_4$$

Example:

1 gram of $NaHSO_3$ solution taken.
Amount of N/10 thio. required = 22 c.c.
Amount of N/10 I consumed by the $NaHSO_3 = 100 - 22 = 78$ c.c.
1 c.c. N/10 I = 0·0052 gram $NaHSO_3$.
Percentage of $NaHSO_3 = \frac{78 \times 0·0052 \times 100}{1} = 40·56$ per cent. $NaHSO_3$.

Sodium hydrosulphite. This body and the compounds which it forms with formaldehyde are frequently used as bleaching agents, giving a more permanent bleach than sulphur dioxide.

Discharging agents.

These substances are in many cases actual bleaching agents, and are used largely in calico printing for the discharging of colour in the printing process. Many chemical substances are in use, but the compounds derived from sodium hydrosulphite have been largely used in recent years owing to their powerful reducing character.

Sodium hydrosulphite, Hydrosulphite B.A.S.F., Hydrosulphite N.F., Rongalite, Hyraldite, Blankite, Formosul, etc. These have been described in Chapters XIX and XXV, pp. 197, 262, and are largely used as discharging agents, and as reducing agents, *e.g.*, in indigo vat dyeing.

Mercerising agents.

The process of mercerising has already been described in the chapter on textile fibres (Chapter XXXIII, p. 312), caustic soda solution being most commonly employed.

Caustic soda, NaOH. This substance is obtained commercially in large quantities from soda ash, or sodium carbonate, by treatment with slaked lime, the solutions being kept dilute and boiling.

$$Na_2CO_3+Ca(OH)_2 \rightarrow 2NaOH+CaCO_3$$

The calcium carbonate is settled and the clear liquor concentrated, the fused caustic being finally run into iron drums.

It is also obtained as a by-product in the manufacture of sodium carbonate by the black ash process.

Electrolytic manufacture of caustic soda. Large quantities are now prepared electrolytically from salt, and many forms of apparatus have been devised for this purpose, and are working successfully, chlorine being simultaneously produced which is converted into bleaching powder.

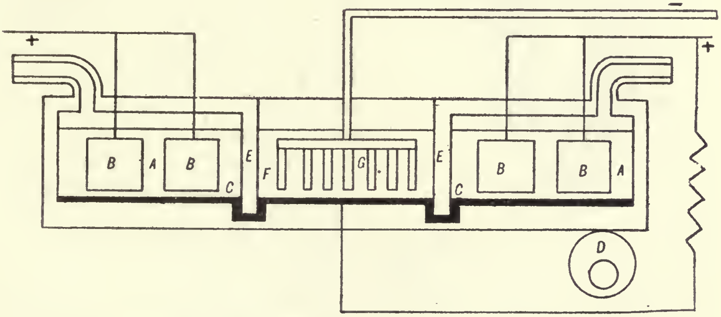


Fig. 98. Castner mercury cell for electrolytic caustic alkali and chlorine.

Castner mercury cell. The apparatus by Castner, shown in Fig. 98, is one of the many types of mercury cells for producing caustic soda, and is one of the most successful. The outer compartment, *A*, contains a 30 per cent. salt solution, with artificial graphite anodes, *B*, and a mercury cathode, *C*, the chlorine being liberated whilst the sodium forms a sodium amalgam.

The cell is given an up and down rocking motion by the eccentric, *D*, which produces a motion in the mercury cathode, and causes the mercury to pass under the partitions or diaphragms, *E*, which dip into grooves or troughs in the base of the cell, the mercury in the troughs forming liquid seals. In the inner compartment, *F*, the mercury acts as the positive electrode, and the sodium ions are transferred through the solution to the iron plate cathodes, *G*, where the ions are discharged, and the sodium dissolves in the water with the production of caustic soda. The inner compartment contains a weak solution of caustic soda, which gradually becomes stronger until it attains a strength of 20 per cent., which may be continuously drawn off. The cells are made up to 6000 H.P., with an efficiency of 90 per cent., and may carry up to 600 amperes at 4 volts.

Townsend cell. This is a successful form of diaphragm cell for the manufacture of electrolytic caustic soda. The cell is formed of cement ends and bottom, *A* (Fig. 99), with diaphragms, *B*, of asbestos, painted with ferric oxide, asbestos fibre and colloidal ferric hydroxide, forming the sides. The cement ends have suitable openings for supplying the salt solution, and leading off the chlorine which is liberated at the carbon anodes, *C*. Each asbestos side is provided with a cathode compartment, *D*, bolted into position against the diaphragm, and the inner surface of each compartment forms a wire gauze cathode, *E*. These compartments contain paraffin oil, which is kept in circulation by the rising bubbles of hydrogen, the sodium dissolving on the wire gauze cathode in the water carried through the diaphragm, by the hydrostatic pressure of the electrolyte in the anode compartment, and the drops of caustic solution collect in the bottoms of the cathode chambers, a 15 per cent. solution passing away through the outlet tubes, *F*. The efficiency of the cell is said to be 90—95 per cent., and works at a voltage of 4 to 5 volts.

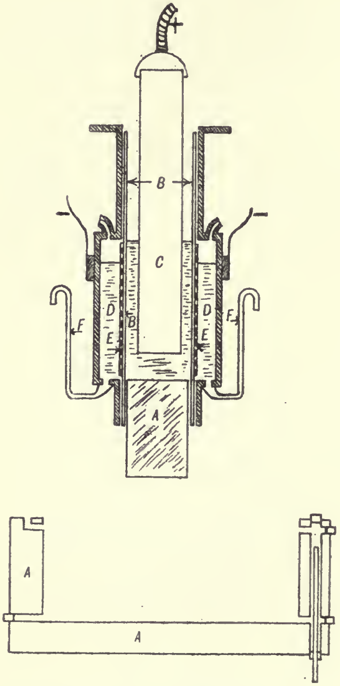


Fig. 99. Townsend electrolytic cell. Manufacture of alkali and chlorine.

The Finlay cell is another very efficient form, in which the electrodes are built up in the form of a filter press, and this form of apparatus may also be used efficiently for the decomposition of water for the production of hydrogen and oxygen, as well as for the production of caustic soda and chlorine. The anode chamber, *A* (Fig. 100), is a wooden framework containing graphite electrodes, and the cast iron cathode chambers, *B*, are separated from the anode chambers by electrolyte chambers. These are formed of a non-porous distance piece, *C*, separating two porous diaphragms, *D*. The various pieces are held together in a frame, *E*, by end pieces in the form of a filter press. By means of holes in the various pieces, ducts above and below are produced when the pieces are screwed together, through which the electrolyte is circulated and the gases escape. The caustic soda produced is thus led off from the outflow cistern, *F*, the gases are removed from the separators, *G*, and salt solution is supplied from the feed cistern, *H*. Caustic liquor up to 15 per cent. in strength may be obtained, the efficiency being 98 per cent. at 3 volts. A 2000 ampere unit measures only $5' \times 2\frac{1}{2}' \times 2'$, so that the apparatus is very compact.

Solid caustic soda is a deliquescent body, very soluble in water, but is liable to become carbonated by the carbon dioxide of the air. It should therefore be excluded from contact with air as far as possible to preserve its strength. The liquors may be recovered from the mercerising process, and also from the subsequent washings, and used again after evaporation to attain the proper strength. This concentration is sometimes effected in vacuum pans. It is also better to treat the liquor with the proper amount of lime to convert the carbonate which may have been formed during the mercerising process back into caustic.

Valuation of caustic soda. The substance may be analysed by the methods described in the chapter on acidimetry and alkalimetry (Chapter XII, pp. 103, 104), the amounts of free caustic and carbonate being determined.

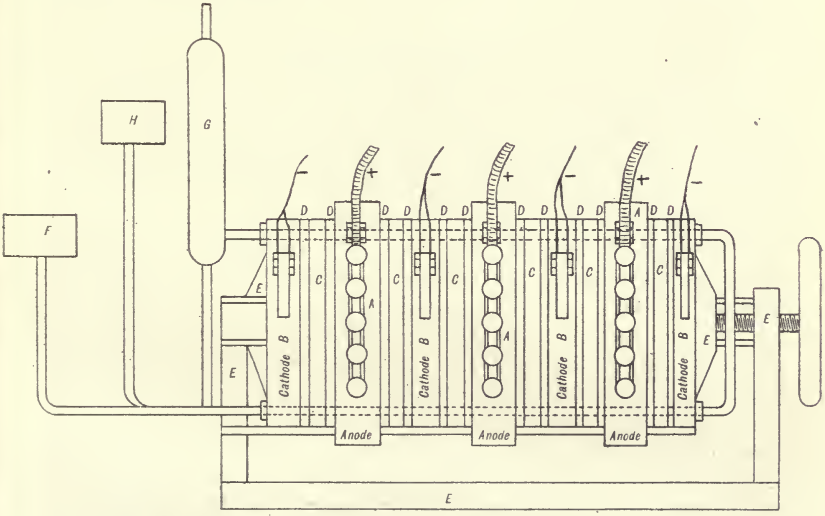


Fig. 100. Finlay electrolytic cell (filter-press form) for manufacture of caustic alkali and chlorine.

CHAPTER XXXVII

MORDANTING AND FIXING AGENTS

IRON MORDANTS: VALUATION OF IRON COMPOUNDS: ALUMINIUM MORDANTS: CHROMIUM MORDANTS: METACHROME MORDANTS: VALUATION OF CHROMIUM MORDANTS: TIN, COPPER, ZINC, ETC., MORDANTS: FIXING AGENTS: ANTIMONY COMPOUNDS AS FIXING AGENTS.

Mordanting agents.

During the processes of dyeing, substances are often used either for fixing the dyestuff on the fibre in the form of an insoluble compound, known as a colour lake, or they may be used for rendering the dyed material faster to washing or to light.

These substances are very largely metallic compounds, which are termed mordants, and a metallic hydroxide is precipitated upon the fibre during the operation of mordanting, the hydroxide afterwards combining with the dyestuff to form an insoluble coloured lake. The metals which fulfil the necessary conditions for successful mordanting, cheapness, colour and insolubility of the colour lake, etc., are comparatively few, and are practically restricted to aluminium, chromium, iron, copper, and tin.

Tannic acid is also employed with basic dyestuffs, though the colour lake produced is soluble in excess of tannic acid, but if the process is followed by treatment with certain metallic substances, insoluble tannates of the metals are produced, which have the power of fixing basic dyestuffs without exerting any solvent action on the colour lake. Antimony compounds possess this property in a high degree, and are frequently termed fixing agents, in distinction from the tannin matter which acts as the mordant. Various special antimony compounds have been put on the market for this purpose.

Iron mordants. The chief salts of iron used as mordants are: ferrous sulphate, ferric sulphate, basic ferric sulphate ("nitrate of iron") and ferrous acetate ("pyrolignite of iron"). These substances have been described in the chapter on sulphur in the case of the sulphates (see Chapter XIX, p. 195), and the acetate is described in Chapter XXVI, p. 268.

Valuation of iron compounds. The amount of ferrous iron may be estimated by titration with N/10 potassium permanganate, in a solution acidified with dilute sulphuric acid, until the liquid is permanently pink.

1 c.c. of N/10 permanganate = 0·0056 gram Fe.

For the estimation of the total iron, the ferric iron is reduced by zinc and then titrated with permanganate. If nitric acid is present a special method has to be adopted. The difference between the total iron and the ferrous iron gives the iron present in the ferric condition.

Aluminium mordants. The principal salts of aluminium employed as mordants are aluminium sulphate, the alums, *e.g.*, potassium and ammonium alums, and aluminium acetate ("red liquor"). These have been described in Chapters XIX and XXVI, to which reference should be made (pp. 195, 268).

Chromium mordants. The chief compounds of chromium which are used as mordants are chrome alum, chromium fluoride, chromium acetate, "chromosol" (a chromium ammonium oxalate), chromium chromate, alkali dichromates and mixtures of potassium dichromate and ammonium sulphate, known as metachrome mordants.

The chief source of chromium is chrome ironstone or chrome iron ore, Cr_2O_3, FeO.

Chromium forms three oxides, chromous oxide, CrO, chromic oxide or sesquioxide, Cr_2O_3, and chromium trioxide or chromic anhydride, CrO_3. The first two act as basic oxides, whilst the third is an acidic oxide, though the one type may be readily converted into the other.

Thus chromic oxide, Cr_2O_3, is readily oxidised into chromic anhydride, CrO_3, thus :

$$Cr_2O_3 + 3O \rightarrow 2CrO_3$$

Chromium salts may therefore be oxidised by suitable means to chromates or dichromates, in which the acidic oxide is CrO_3 ; or, again, chromates or dichromates may be reduced by suitable means to chromium salts, in which the chromium is present as the basic chromic oxide, oxygen being withdrawn and the action above being reversed.

Chromium sulphate, $Cr_2(SO_4)_3$ may be produced by the solution of precipitated chromic hydroxide in sulphuric acid, thus :

$$2Cr(OH)_3 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 6H_2O$$

When combined with a molecular quantity of an alkali sulphate, it gives rise to an alum.

Chrome alum, $Cr_2(SO_4)_3$, K_2SO_4, $24H_2O$. Potassium dichromate is reduced by sulphur dioxide or other suitable reducing agent in the presence of sulphuric acid, and the chrome alum crystallised from the solution. It is often difficult to crystallise the salt, and it is therefore best to seed the solution with a small crystal of the substance.

$$K_2Cr_2O_7 + 3SO_2 + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

Chromium fluoride, $CrF_3, 4H_2O$. This may be prepared as a green crystalline substance by dissolving chromic oxide in hydrofluoric acid. It is easily soluble in water, but has a corrosive action on glass. It is useful in mordanting both wool and cotton.

Chromium acetate, $Cr(C_2H_3O_2)_3$. This is prepared similarly to aluminium acetate, see Chapter XXVI, p. 268. It is little used as a mordant in cotton and wool dyeing, but is extensively employed in printing processes.

"Chromosol." A double oxalate of chromium and ammonium is put on the market under the name of "chromosol" for mordanting purposes.

Potassium dichromate, $K_2Cr_2O_7$. In this compound the chromium is present as the acidic oxide, CrO_3. It is prepared by roasting chrome iron ore with potassium carbonate and lime.

$$2(Cr_2O_3, FeO) + 3K_2CO_3 + CaO + 7O \rightarrow 3K_2CrO_4 + CaCrO_4 + Fe_2O_3 + 3CO_2$$

The yellow potassium chromate is extracted with water, and treated with potassium sulphate to convert the lime compound into potassium chromate.

$$CaCrO_4 + K_2SO_4 \rightarrow CaSO_4 + K_2CrO_4$$

The potassium chromate by treatment with sulphuric acid is converted into the dichromate, which may be crystallised from the solution.

$$2K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$$

Sodium dichromate, $Na_2Cr_2O_7, 2H_2O$, is prepared similarly to the potassium compound, and is usually employed instead of the potassium salt, as it is cheaper and more soluble in water.

The dichromates are powerful oxidising agents, one molecule of the substance yielding three atoms of oxygen available for oxidation in the presence of sulphuric acid.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

This action is often made use of in the production of a powerful oxidising mixture.

Metachrome mordants. Potassium dichromate, mixed with ammonium sulphate, is sold under the name metachrome mordant for the purpose of after-chroming, in which the dyeing and mordanting are done in a single bath.

Chromium chromate, $Cr_2(CrO_4)_3, 9H_2O$, and basic compounds of this salt, used for mordanting, are prepared by dissolving chromic hydroxide in chromic acid and crystallising.

$$2Cr(OH)_3 + 3H_2CrO_4 \rightarrow Cr_2(CrO_4)_3 + 6H_2O$$

Valuation of dichromates. The oxidation of iron salts is made use of for the valuation of dichromates, the iron salt being preferably used in the form of granular ferrous ammonium sulphate, $FeSO_4, (NH_4)_2SO_4, 6H_2O$, as this salt can be obtained in a very pure condition.

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + K_2SO_4 + 3Fe_2(SO_4)_3 + 7H_2O$$

N/10 ferrous ammonium sulphate is prepared (39·2 grams per litre), and 25 c.c. of this solution is taken for the titration.

5 grams of the dichromate to be tested are weighed out, dissolved in 1 litre of water, and this solution is added from a burette to 25 c.c. of the iron solution until the iron is completely oxidised to the ferric condition.

The end point of the reaction is ascertained by taking a drop of the solution on a glass rod, and mixing with a drop of **freshly prepared** potassium **ferricyanide** solution (about 0·1 per cent.) on a white tile. A blue coloration will be given as long as ferrous iron is present, and the end point is indicated by the blue colour being no longer given.

Example.

5 grams of $K_2Cr_2O_7$ dissolved in 1000 c.c. of water.
Added to 25 c.c. of N/10 ferrous solution.
26 c.c. of $K_2Cr_2O_7$ required.
1 c.c. N/10 iron solution = 0·0049 gram of $K_2Cr_2O_7$.
25 ,, ,, ,, ,, = 0·0049 × 25 gram of $K_2Cr_2O_7$
= 0·1225 gram $K_2Cr_2O_7$.
26 c.c. $K_2Cr_2O_7$ contain 0·1225 gram $K_2Cr_2O_7$.
1000 c.c. $K_2Cr_2O_7$ contain 4·71 grams ,,
5 grams of sample contain 4·71 ,, ,,
100 ,, ,, ,, ,, 94·2 ,, ,,
94·2 per cent. $K_2Cr_2O_7$.

Tin, copper, etc., mordants. **Stannous chloride (tin crystals** or **tin salt), stannic chloride,** and **copper sulphate** have already been described in Chapters XVIII and XIX (pp. 172, 194).

Sodium stannate (preparing salt), Na_2SnO_3, $3H_2O$. In this compound stannic oxide, SnO_2, acts in the acidic condition, and the compound may be prepared by fusing this substance with sodium carbonate, thus:

$$SnO_2 + Na_2CO_3 \rightarrow Na_2SnO_3 + CO_2$$

It is used as a mordant, and is very largely used in calico printing.

Zinc, nickel, and other metallic salts, have also been used as mordants, but are not of such importance as those already dealt with.

Tannin mordants. **Tannic acid,** and **tannin matters,** have been dealt with very fully in Chapter XXXII (p. 306), and also their use as mordants.

Fixing agents.

Antimony compounds. The use of antimony compounds as fixing agents in dyeing cotton with basic dyestuffs after treatment with tannin has been already referred to under tannin matters in Chapter XXXII (p. 307).

The chief compounds used are **antimony fluoride**, SbF_3, prepared from antimonious oxide, Sb_4O_6, and hydrofluoric acid, or double salts of this compound, such as the so-called commercial **antimony salt**, SbF_3, $(NH_4)_2SO_4$, and **double antimony fluoride**, SbF_3, NaF.

Tartar emetic. This salt is the most important of the antimony compounds, and has been more used than any other of the antimony salts as a fixing agent. It is described in Chapter XXX (p. 291). The corresponding sodium compound, sodium antimonyl tartrate, similar to the potassium compound in composition and preparation, has also been used.

Other compounds used are **antimony oxalate**, and **patent antimony salt** (Chapter XXX, pp. 289, 290); **antimonine**, an antimony lactate (Chapter XXX, p. 288), and **antimony tannate** (Chapter XXXII, p. 307).

CHAPTER XXXVIII

DRESSING, FINISHING, WEIGHTING, WATERPROOFING AND FIREPROOFING MATERIALS

STIFFENING MATERIALS: FLOUR, STARCH, DEXTRIN, GUMS. SOFTENING AGENTS: OILS, FATS, WAXES, GLYCERINE, HYGROSCOPIC SALTS. WEIGHTING AND FILLING MATERIALS: METALLIC SALTS, CHINA CLAY, SILICATES, ETC. ANTISEPTIC DRESSINGS: CARBOLIC AND SALICYLIC ACIDS. WATERPROOFING MATERIALS: ALUMINIUM COMPOUNDS, CELLULOSE ACETATE FOR AEROPLANE FABRICS. FIREPROOFING MATERIALS: SODIUM TUNGSTATE, WATER GLASS.

Many fabrics after being woven receive a final treatment to improve the colour, handle, appearance and weight. This treatment, apart from bleaching and dyeing, is known under the general name of finishing. This term comprises a large number of processes, which differ according to the cloth under treatment, and the characteristics required in the finished article.

Some processes only affect the state of the fibres, whilst others introduce substances into the cloth, in some cases for giving waterproof or fireproof qualities.

The various substances employed may be divided into the following main classes: (1) materials for improving the stiffness of the material, and for binding other substances to the fabrics; (2) materials for improving the "handle," generally known as softening agents; (3) materials for weighting, by filling the pores in the fabric, and known as filling and weighting agents; (4) materials possessing antiseptic properties; (5) materials for waterproofing; (6) materials for rendering the fabric non-inflammable.

(1) **Stiffening materials.** The chief substances in this class are flour, starch, dextrin and gums.

Flour. For finishing purposes generally, the flour made from wheat is superior to that made from any other grain since it has much better binding properties. The chief substances present in wheat flour are starch and gluten. The gluten which is present has a big effect on the binding power of the starch, and is present in wheat flour to a greater extent than in the flour from other cereals. The starch can be removed by placing the flour in a bag and squeezing it under water, the gluten remaining in the bag. In this way the gluten content of the flour can be ascertained.

Starch. There are many varieties of starch, according to the source from which the starch is obtained. The commonest varieties are those obtained from wheat, rice, maize and potatoes, the different varieties being readily detected by examination under the microscope. The starch is composed of small granules which differ in shape and size according to the variety of the starch. The extraction of this material, and its properties, have already been dealt with in Chapter XXXI (see p. 295).

Fabrics are treated by dipping in a dilute solution of starch paste, then partially drying and, whilst slightly damp, passing them over hot rollers. The starch stiffens the fibres, and gives them a much better appearance and "handle." Similar effects can be obtained by treating the fabrics with a suspension of starch in cold water, and afterwards passing them between hot rollers whilst still wet. This process is used when a high degree of stiffness is required and is used for linen collars, etc.

Dextrin. Dextrin is used as a binding agent, but is also used alone for producing a bright stiff finish on articles which would otherwise be very limp, such as lace, etc. Dextrin can readily be distinguished from starch by its reaction with a solution of iodine. The substance has already been dealt with in Chapter XXXI (see p. 298).

Gums. These are used in great variety for producing bright stiff finishes. They consist of the dried sap of certain tropical plants. The principal varieties employed in the textile industries have already been dealt with in Chapter XXXI (see p. 298).

(2) **Softening agents.** The substances of this class are of very great variety, but the principal ones are oils, fats, tallow (prepared from beef and mutton fat, p. 269), waxes, and soaps, sometimes glycerine, and certain hygroscopic salts, such as magnesium and zinc chlorides. Their chief use is to improve the "handle" of the fabric, and also to hold the filling agents on the fibre. The bodies have mostly been dealt with in previous chapters, and reference should be made to these parts.

(3) **Weighting and filling agents.** The chief substances in this class are metallic salts, the most important bodies used being magnesium, zinc, calcium and barium chlorides (Chapter XVIII, p. 170), alum (Chapter XIX, p. 195), barium, magnesium and sodium sulphates (Chapter XIX, pp. 193, 194), magnesium carbonate (Chapter XX, p. 204), china clay (Chapter XX, p. 217), and sodium silicate—"water glass" (Chapter XX, p. 216). These substances have been dealt with in the previous chapters mentioned above.

Some of these compounds, such as zinc and magnesium chlorides, are hygroscopic, consequently materials containing them which are dressed with starch always feel soft.

(4) **Antiseptic dressings.** Many of the bodies already described, such as zinc and magnesium chlorides, are used as antiseptic dressings for preventing the formation of mould and fungi in the materials, such as flour, starch, tallow, which are very liable to turn mouldy in the presence of moisture.

Many other bodies may be used, such as formic acid, boric acid, borax, camphor, but carbolic acid or phenol (Chapter XXXII, p. 305), and salicylic acid (Chapter XXXII, p. 306) are among the best substances which may be employed. The use of salicylic acid is particularly advantageous as the acid is non-corrosive and has no odour, whilst 1 part per 1000 in the dressing used will prevent all possibility of mouldiness, avoid any objectionable odours in the material, and preserve the textile fabric.

(5) **Waterproofing materials.** Fabrics can be rendered waterproof by a variety of methods, the most efficient probably being the process in which the fabric is coated with a fine sheet of india rubber.

Willesden goods. The methods of making waterproof cotton fabrics by treating with an ammoniacal solution of cupric oxide have already been described in Chapter XXXI (p. 296).

Aluminium compounds, waxes, and resins for waterproofing. Other methods consist in depositing water-repelling substances in the fibres. The chief substances used for this purpose are metallic oxides and the most commonly employed is alumina.

The alumina is taken up by the fibre in the form of salts which are subsequently decomposed either by chemicals or by heat, leaving the alumina precipitated inside the fabric. Alum and aluminium sulphate can both be used, the alumina being precipitated by means of alkalis, thus :

$$Al_2(SO_4)_3 + 6NaOH \rightarrow 3Na_2SO_4 + Al_2(OH)_6$$

It is, however, better to use aluminium acetate, which can be decomposed by steam, thus :

$$2(CH_3 . COO)_3Al + 6H_2O \rightarrow Al_2(OH)_6 + 6CH_3 . COOH$$

The acetic acid being volatile in steam is carried away.

Other substances, such as waxes and resins, are sometimes used for waterproofing fabrics. Waxes are applied either in the molten state, or in benzene solution, the solvent being evaporated and depositing the wax on the fibre. Resins are dissolved in spirit or in alkalis. In the latter case a subsequent treatment with acids is necessary to render the resins insoluble.

Cellulose acetate for waterproofing. Cellulose acetate dissolved in tetrachloro-ethane and methyl or ethyl alcohols is used for giving a varnish or coating to certain materials, and render them waterproof. This material has been used as a **"dope" for aeroplane fabrics** to render them impermeable.

Suitable mixtures given by Clement and Rivière (see *Journ. Soc. Chem. Ind.*, 1915, 75) are (1) tetrachloro-ethane, 900 parts, denatured 95 per cent. alcohol, 100 parts, and cellulose acetate, 75 parts; (2) tetrachloro-ethane, 800 parts, denatured 95 per cent. alcohol, 80 parts, acetone, 120 parts, and cellulose acetate, 65 parts.

Two or three coats of about 500 grams per sq. metre are applied to the stretched fabric, which is then said to possess advantages over rubbered material as regards impermeability to water, oil and motor spirit.

Cellulose acetate has also been suggested for manufacturing artificial silk, and for use as a thickening agent instead of gum or starch in the textile printing industry, and as a resist in dyeing.

(6) **Fireproofing materials**. The object of these dressings is to render the material non-inflammable, and the application of these bodies might with advantage be more widely adopted. Most salts which readily melt at a low temperature, forming a coating over the fibre, are suitable, such as alum, borax, ammonium phosphate, sodium silicate (water glass), magnesium salts and sodium tungstate, Na_2WO_4. The latter compound gives probably the best result, and is prepared by fusing the mineral, **Wolfram** (tungstate of iron), with sodium carbonate and extracting with water. It has the advantage that the colours and fibres are not affected by it, but its chief disadvantage is the question of cost. It has also found application in the weighting of silk.

APPENDIX

Twaddell (Tw.) into *specific gravity* $= \frac{0\cdot 5n + 100}{100}$.

Baumé (Rational scale) in common use on the Continent.

For liquids *heavier* than water B ° into sp. gr. $= \frac{144\cdot 3}{144\cdot 3 - n}$.

For liquids *lighter* than water B.° into sp. gr. $= \frac{144\cdot 3}{144\cdot 3 + n}$.

TABLE I.

COMPARISON OF HYDROMETER SCALES.

(*Baumé* (*Rational*), *Twaddell and Specific Gravity.*)

Tw.	B.	Sp. gr.	Tw.	B.	Sp. gr.	Tw.	B.	Sp. gr.	Tw.	B.	Sp. gr.
0	0	1·000	44	26·0	1·220	88	44·1	1·440	132	57·4	1·660
1	0·7	1·005	45	26·4	1·225	89	44·4	1·445	133	57·7	1·665
2	1·4	1·010	46	26·9	1·230	90	44·8	1·450	134	57·9	1·670
3	2·1	1·015	47	27·4	1·235	91	45·1	1·455	135	58·2	1·675
4	2·7	1·020	48	27·9	1·240	92	45·4	1·460	136	58·4	1·680
5	3·4	1·025	49	28·4	1·245	93	45·8	1·465	137	58·7	1·685
6	4·1	1·030	50	28·8	1·250	94	46·1	1·470	138	58·9	1·690
7	4·7	1·035	51	29·3	1·255	95	46·4	1·475	139	59·2	1·695
8	5·4	1·040	52	29·7	1·260	96	46·8	1·480	140	59·5	1·700
9	6·0	1·045	53	30·2	1·265	97	47·1	1·485	141	59·7	1·705
10	6·7	1·050	54	30·6	1·270	98	47·4	1·490	142	60·0	1·710
11	7·4	1·055	55	31·1	1·275	99	47·8	1·495	143	60·2	1·715
12	8·0	1·060	56	31·5	1·280	100	48·1	1·500	144	60·4	1·720
13	8·7	1·065	57	32·0	1·285	101	48·4	1·505	145	60·6	1·725
14	9·4	1·070	58	32·4	1·290	102	48·7	1·510	146	60·9	1·730
15	10·0	1·075	59	32·8	1·295	103	49·0	1·515	147	61·1	1·735
16	10·6	1·080	60	33·3	1·300	104	49·4	1·520	148	61·4	1·740
17	11·2	1·085	61	33·7	1·305	105	49·7	1·525	149	61·6	1·745
18	11·9	1·090	62	34·2	1·310	106	50·0	1·530	150	61·8	1·750
19	12·4	1·095	63	34·6	1·315	107	50·3	1·535	151	62·1	1·755
20	13·0	1·100	64	35·0	1·320	108	50·6	1·540	152	62·3	1·760
21	13·6	1·105	65	35·4	1·325	109	50·9	1·545	153	62·5	1·765
22	14·2	1·110	66	35·8	1·330	110	51·2	1·550	154	62·8	1·770
23	14·9	1·115	67	36·2	1·335	111	51·5	1·555	155	63·0	1·775
24	15·4	1·120	68	36·6	1·340	112	51·8	1·560	156	63·2	1·780
25	16·0	1·125	69	37·0	1·345	113	52·1	1·565	157	63·5	1·785
26	16·5	1·130	70	37·4	1·350	114	52·4	1·570	158	63·7	1·790
27	17·1	1·135	71	37·8	1·355	115	52·7	1·575	159	64·0	1·795
28	17·7	1·140	72	38·2	1·360	116	53·0	1·580	160	64·2	1·800
29	18·3	1·145	73	38·6	1·365	117	53·3	1·585	161	64·4	1·805
30	18·8	1·150	74	39·0	1·370	118	53·6	1·590	162	64·6	1·810
31	19·3	1·155	75	39·4	1·375	119	53·9	1·595	163	64·8	1·815
32	19·8	1·160	76	39·8	1·380	120	54·1	1·600	164	65·0	1·820
33	20·3	1·165	77	40·1	1·385	121	54·4	1·605	165	65·2	1·825
34	20·9	1·170	78	40·5	1·390	122	54·7	1·610	166	65·5	1·830
35	21·4	1·175	79	40·8	1·395	123	55·0	1·615	167	65·7	1·835
36	22·0	1·180	80	41·2	1·400	124	55·2	1·620	168	65·9	1·840
37	22·5	1·185	81	41·6	1·405	125	55·5	1·625	169	66·1	1·845
38	23·0	1·190	82	42·0	1·410	126	55·8	1·630	170	66·3	1·850
39	23·5	1·195	83	42·3	1·415	127	56·0	1·635	171	66·5	1·855
40	24·0	1·200	84	42·7	1·420	128	56·3	1·640	172	66·7	1·860
41	24·5	1·205	85	43·1	1·425	129	56·6	1·645	173	67·0	1·865
42	25·0	1·210	86	43·4	1·430	130	56·9	1·650			
43	25·5	1·215	87	43·8	1·435	131	57·1	1·655			

TABLE II.

PRESSURE OF WATER VAPOUR IN MM. OF MERCURY FROM – 20° TO 230° C.

Temp. C.	mm. of Hg.	Temp. C.	mm. of Hg.
– 20	0·92	40	54·91
– 5	3·17	45	71·39
0	4·58	50	91·98
+ 5	6·53	55	117·48
10	9·16	60	148·79
11	9·79	70	233·09
12	10·46	80	354·64
13	11·16	90	525·69
14	11·91	100	760
15	12·70	105	1·2 atmos.
16	13·54	110	1·41 ,,
17	14·42	115	1·67 ,,
18	15·36	120	1·94 ,,
19	16·35	125	2·29 ,,
20	17·39	130	2·6 ,,
21	18·49	140	3·6 ,,
22	19·66	150	4·7 ,,
23	20·89	160	6·1 ,,
24	22·18	170	7·8 ,,
25	23·55	180	9·9 ,,
26	24·99	190	12·4 ,,
27	26·50	200	15·3 ,,
28	28·10	210	18·8 ,,
29	29·78	220	22·9 ,,
30	31·55	230	27·5 ,,
35	41·83		

TABLE III.

Pressure of Water Vapour in mm. of mercury from 0° to 212° F.

Temp. F.	mm.	Temp. F.	mm.	Temp. F.	mm.	Temp. F.	mm.
0	1·15	33	4·75	66	16·25	99	47·24
1	1·21	34	4·96	67	16·76	100	48·81
2	1·26	35	5·14	68	17·39	101	50·16
3	1·33	36	5·36	69	17·94	102	51·81
4	1·38	37	5·55	70	18·61	103	53·22
5	1·45	38	5·79	71	19·31	104	54·91
6	1·52	39	6·05	72	19·90	105	56·76
7	1·58	40	6·26	73	20·63	106	58·29
8	1·66	41	6·53	74	21·26	107	60·17
9	1·73	42	6·76	75	22·04	108	61·78
10	1·81	43	7·04	76	22·71	109	63·76
11	1·89	44	7·34	77	23·54	110	65·45
12	1·98	45	7·60	78	24·26	111	67·54
13	2·06	46	7·90	79	25·14	112	69·32
14	2·16	47	8·17	80	26·04	113	71·39
15	2·26	48	8·52	81	26·82	114	73·75
16	2·35	49	8·80	82	27·78	115	75·67
17	2·40	50	9·16	83	28·60	116	78·03
18	2·58	51	9·47	84	29·61	117	80·04
19	2·68	52	9·85	85	30·48	118	82·52
20	2·80	53	10·18	86	31·55	119	84·63
21	2·91	54	10·60	87	32·47	120	87·23
22	3·05	55	11·02	88	33·61	130	114·41
23	3·17	56	11·39	89	34·77	140	149·21
24	3·31	57	11·84	90	35·77	150	191·76
25	3·44	58	12·23	91	37·01	160	245·17
26	3·60	59	12·70	92	38·06	170	310·54
27	3·73	60	13·12	93	39·36	180	388·34
28	3·90	61	13·63	94	40·48	190	483·6
29	4·07	62	14·07	95	41·83	200	595·4
30	4·26	63	14·61	96	43·03	210	730·6
31	4·41	64	15·17	97	44·48	212	760·0
32	4·58	65	15·66	98	45·97		

TABLE IV.

DETERMINATION OF RELATIVE HUMIDITY.

Centigrade Table of Vapour Pressures for Wet and Dry Bulb Thermometers.

t°	D°= Differences in temperature Centigrade between wet and dry bulbs										
	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°	10°
0°	4·6	3·7	2·9	2·1	1·3						
1°	4·9	4·1	3·2	2·4	1·6						
2°	5·3	4·4	3·6	2·7	1·9	1·1	0·3				
3°	5·7	4·8	3·9	3·1	2·2	1·4	0·6				
4°	6·1	5·2	4·3	3·4	2·6	1·8	0·9				
5°	6·5	5·6	4·7	3·8	2·9	2·1	1·2				
6°	7·0	6·0	5·1	4·2	3·3	2·4	1·6				
7°	7·5	6·5	5·5	4·6	3·7	2·8	1·9	1·1	0·2		
8°	8·3	7·0	6·0	5·0	4·1	3·2	2·3	1·4	0·6		
9°	8·6	7·5	6·5	5·5	4·5	3·6	2·7	1·8	0·9		
10°	9·2	8·1	7·0	6·0	5·0	4·0	3·1	2·2	1·3		
11°	9·8	8·7	7·6	6·5	5·5	4·5	3·5	2·6	1·7		
12°	10·5	9·3	8·2	7·1	6·0	5·0	4·0	3·0	2·1	1·2	0·3
13°	11·2	10·0	8·9	7·6	6·5	5·5	4·5	3·5	2·5	1·6	0·7
14°	11·9	10·7	9·4	8·3	7·1	6·1	5·0	4·0	3·0	2·0	1·1
15°	12·7	11·4	10·1	9·0	7·8	6·6	5·5	4·5	3·4	2·5	1·5
16°	13·5	12·2	10·9	9·7	8·4	7·3	6·0	5·0	4·0	3·0	1·9
17°	14·4	13·0	11·7	10·4	9·1	8·0	6·7	5·6	4·5	3·5	2·4
18°	15·4	13·9	12·5	11·2	9·9	8·6	7·4	6·3	5·1	4·0	3·0
19°	16·3	14·9	13·4	12·0	10·7	9·4	8·1	6·9	5·7	4·6	3·5
20°	17·4	15·9	14·3	12·9	11·5	10·2	8·8	7·6	6·4	5·2	4·1
21°	18·5	16·9	15·3	13·8	12·4	11·0	9·6	8·4	7·1	5·7	4·7
22°	19·7	18·0	16·4	14·8	13·3	11·9	10·5	9·1	7·8	6·6	5·4
23°	20·9	19·2	17·5	15·9	14·3	12·8	11·3	10·0	8·6	7·3	6·1
24°	22·2	20·4	18·6	17·0	15·3	13·8	12·3	10·9	9·4	8·1	6·8
25°	23·5	21·7	19·9	18·1	16·4	14·8	13·3	11·8	10·3	9·0	7·6

TABLE V.

Table of Vapour Pressures in mm. of mercury for various differences of Dry and Wet Bulbs (Fahr.).

Dry bulb temp. F.	Difference between dry and wet bulbs in degrees Fahrenheit									
	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
32°	4·6	4·1	3·7	3·2	2·8	2·3	1·9	1·4	1·0	0·5
34	5·0	4·5	4·1	3·6	3·2	2·7	2·3	1·8	1·4	0·9
36	5·4	4·9	4·4	3·9	3·5	3·0	2·6	2·1	1·7	1·2
38	5·8	5·3	4·8	4·3	3·8	3·3	2·8	2·3	1·9	1·5
40	6·3	5·8	5·3	4·8	4·3	3·8	3·3	2·8	2·4	1·9
42	6·8	6·3	5·8	5·3	4·8	4·3	3·8	3·3	2·8	2·3
44	7·3	6·8	6·3	5·8	5·3	4·7	4·2	3·7	3·2	2·7
46	7·9	7·4	6·8	6·3	5·7	5·2	4·6	4·1	3·6	3·1
48	8·5	7·9	7·3	6·8	6·2	5·7	5·1	4·6	4·1	3·5
50	9·2	8·6	8·0	7·4	6·8	6·2	5·6	5·1	4·6	4·0
52	9·9	9·3	8·7	8·1	7·5	6·9	6·3	5·7	5·1	4·5
54	10·6	10·0	9·4	8·8	8·2	7·6	6·9	6·3	5·7	5·1
56	11·4	10·8	10·2	9·5	8·9	8·2	7·6	7·0	6·3	5·7
58	12·2	11·5	10·9	10·2	9·6	8·9	8·3	7·6	7·0	6·3
60	13·1	12·4	11·8	11·1	10·4	9·6	9·0	8·4	7·7	7·0
62	14·1	13·4	12·7	12·0	11·3	10·6	9·9	9·2	8·5	7·8
64	15·2	14·4	13·7	13·0	12·2	11·4	10·7	10·0	9·3	8·6
66	16·3	15·5	14·7	14·0	13·2	12·4	11·6	10·8	10·1	9·4
68	17·4	16·6	15·8	15·0	14·2	13·4	12·6	11·8	11·0	10·2
70	18·6	17·8	17·0	16·2	15·3	14·5	13·7	12·8	12·0	11·2
72	19·9	19·0	18·2	17·3	16·5	15·6	14·8	13·9	13·2	12·2
74	21·3	20·4	19·5	18·6	17·7	16·8	15·9	15·0	14·1	13·2
76	22·7	21·8	20·8	19·9	18·9	18·0	17·0	16·1	15·1	14·2
78	24·3	23·3	22·3	21·3	20·3	19·3	18·3	17·3	16·3	15·4
80	26·0	25·0	24·0	23·0	22·0	20·9	19·9	18·9	17·9	16·9
82	27·7	26·6	25·6	24·5	23·5	22·4	21·4	20·3	19·3	18·3
84	29·6	28·5	27·4	26·3	25·2	24·1	23·0	21·9	20·8	19·6
86	31·5	30·3	29·1	28·0	26·8	25·7	24·5	23·3	22·2	21·0
88	33·6	32·3	31·0	29·7	28·5	27·3	26·1	24·9	23·8	22·7
90	35·8	34·4	33·0	31·6	30·3	29·0	27·8	26·6	25·4	24·3
92	38·1	36·6	35·2	33·8	32·4	31·0	29·8	28·6	27·4	26·2
94	40·5	39·0	37·5	35·9	34·5	33·1	31·8	30·5	29·2	28·0
96	43·0	41·4	39·9	38·3	36·8	35·3	33·9	32·6	31·3	30·0
98	46·0	44·3	42·7	41·1	39·5	37·9	36·4	35·0	33·6	32·2
100	48·8	47·1	45·4	43·7	42·1	40·5	39·0	37·5	36·0	34·5

TABLE V (*continued*).

Dry bulb temp. F.	Difference between dry and wet bulbs in degrees Fahrenheit								
	10°	11°	12°	13°	14°	15°	16°	17°	18°
32°									
34	0·5								
36	0·8	0·5							
38	1·1	0·9	0·5						
40	1·5	1·2	0·9	0·5					
42	1·9	1·5	1·1	0·7					
44	2·3	1·8	1·4	1·0	0·5				
46	2·6	2·1	1·6	1·2	0·8				
48	2·9	2·4	2·0	1·5	1·0	0·5			
50	3·4	2·9	2·4	1·9	1·5	1·0	0·5		
52	3·9	3·5	2·9	2·4	1·9	1·4	0·9	0·5	
54	4·5	4·0	3·4	2·8	2·3	1·8	1·3	0·9	0·5
56	5·0	4·4	3·8	3·2	2·7	2·2	1·7	1·3	0·9
58	5·6	5·0	4·4	3·8	3·3	2·8	2·3	1·8	1·3
60	6·4	5·8	5·2	4·6	4·0	3·4	2·9	2·2	1·7
62	7·1	6·5	5·9	5·3	4·7	4·1	3·5	2·9	2·3
64	7·9	7·2	6·5	5·9	5·3	4·7	4·1	3·5	2·9
66	8·7	8·0	7·3	6·6	5·9	5·3	4·7	4·1	3·5
68	9·5	8·8	8·1	7·4	6·7	6·0	5·3	4·7	4·1
70	10·4	9·7	9·0	8·3	7·6	6·9	6·2	5·5	4·8
72	11·4	10·6	9·8	9·1	8·4	7·7	7·0	6·3	5·6
74	12·4	11·6	10·8	10·0	9·2	8·5	7·8	7·1	6·4
76	13·4	12·6	11·8	11·0	10·2	9·4	8·6	7·9	7·2
78	14·5	13·7	12·9	12·1	11·3	10·5	9·7	8·9	8·1
80	15·9	15·0	14·1	13·2	12·3	11·5	10·7	9·9	9·1
82	17·3	16·4	15·5	14·6	13·7	12·8	11·9	11·0	10·1
84	18·6	17·6	16·6	15·6	14·7	13·8	12·9	12·0	11·1
86	20·0	19·0	18·0	17·0	16·0	15·0	14·1	13·2	12·3
88	21·6	20·5	19·4	18·3	17·2	16·2	15·2	14·2	13·2
90	23·2	22·0	20·9	19·8	18·7	17·6	16·5	15·4	14·3
92	25·0	23·8	22·6	21·4	20·2	19·1	18·0	16·9	15·8
94	26·8	25·5	24·3	23·1	21·9	20·7	19·5	18·3	17·1
96	28·7	27·4	26·1	24·8	23·6	22·4	21·2	20·2	18·8
98	30·8	29·4	28·1	26·8	25·5	24·2	22·9	21·6	20·3
100	33·0	31·6	30·2	28·8	27·5	26·2	24·9	23·6	22·3

NOTE. For intermediate dry bulb temperatures, take the mean of adjacent figures in vertical columns, *e.g.*, 51° F. dry bulb, diff. 5°

$$\frac{6{\cdot}2+6{\cdot}9}{2}=6{\cdot}55 \text{ mm.}$$

TABLE VI.

SP. GR. $\left(\frac{15^\circ}{4^\circ}\right)$ AND STRENGTHS OF HYDROCHLORIC ACID SOLUTIONS.

Parts by weight of HCl *in* 100 *parts by weight of solution.*

Sp. gr.	HCl	Sp. gr.	HCl	Sp. gr.	HCl	Sp. gr.	HCl
1·000	0·16	1·055	11·18	1·105	20·97	1·155	30·55
1·005	1·15	1·060	12·19	1·110	21·92	1·160	31·52
1·010	2·14	1·065	13·19	1·115	22·86	1·165	32·49
1·015	3·12	1·070	14·17	1·120	23·82	1·170	33·46
1·020	4·13	1·075	15·16	1·125	24·78	1·175	34·42
1·025	5·15	1·080	16·15	1·130	25·75	1·180	35·59
1·030	6·15	1·085	17·13	1·135	26·70	1·185	36·31
1·035	7·15	1·090	18·11	1·140	27·66	1·190	37·23
1·040	8·16	1·095	19·06	1·145	28·61	1·195	38·16
1·045	9·16	1·100	20·01	1·150	29·57	1·200	39·11
1·050	10·17						

TABLE VII.

SP. GR. $\left(\frac{15^\circ}{4^\circ}\right)$ AND STRENGTHS OF NITRIC ACID SOLUTIONS.

Parts by weight of HNO_3 *in* 100 *parts by weight of solution.*

Sp. gr.	HNO_3	Sp. gr.	HNO_3	Sp. gr.	HNO_3	Sp. gr.	HNO_3
1·000	0·10	1·135	22·54	1·265	42·10	1·395	64·25
1·005	0·20	1·140	23·31	1·270	42·87	1·400	65·30
1·010	1·90	1·145	24·08	1·275	43·64	1·405	66·40
1·015	2·80	1·150	24·84	1·280	44·41	1·410	67·50
1·020	3·70	1·155	25·60	1·285	45·18	1·415	68·63
1·025	4·60	1·160	26·36	1·290	45·95	1·420	69·80
1·030	5·50	1·165	27·12	1·295	46·72	1·425	70·98
1·035	6·38	1·170	27·88	1·300	47·49	1·430	72·17
1·040	7·26	1·175	28·63	1·305	48·26	1·435	73·39
1·045	8·13	1·180	29·38	1·310	49·07	1·440	74·68
1·050	8·99	1·185	30·13	1·315	49·89	1·445	75·98
1·055	9·84	1·190	30·88	1·320	50·71	1·450	77·28
1·060	10·68	1·195	31·62	1·325	51·53	1·455	78·60
1·065	11·51	1·200	32·36	1·330	52·37	1·460	79·98
1·070	12·33	1·205	33·09	1·335	53·22	1·465	81·42
1·075	13·15	1·210	33·82	1·340	54·07	1·470	82·90
1·080	13·95	1·215	34·55	1·345	54·93	1·475	84·45
1·085	14·74	1·220	35·28	1·350	55·79	1·480	86·05
1·090	15·53	1·225	36·03	1·355	56·66	1·485	87·70
1·095	16·32	1·230	36·78	1·360	57·57	1·490	89·60
1·100	17·11	1·235	37·53	1·365	58·48	1·495	91·60
1·105	17·89	1·240	38·29	1·370	59·39	1·500	94·09
1·110	18·67	1·245	39·05	1·375	60·30	1·505	96·39
1·115	19·45	1·250	39·82	1·380	61·27	1·510	98·10
1·120	20·33	1·255	40·58	1·385	62·24	1·515	99·07
1·125	21·00	1·260	41·34	1·390	63·23	1·520	99·67
1·130	21·77						

TABLE VIII.

SP. GR. $\left(\frac{15^\circ}{4^\circ}\right)$ AND STRENGTHS OF SULPHURIC ACID SOLUTIONS (LUNGE).

Parts by weight of H_2SO_4 *in* 100 *parts by weight of solution.*

Sp.gr.	H_2SO_4	Sp.gr.	H_2SO_4	Sp.gr.	H_2SO_4	Sp. gr.	H_2SO_4
1·00	0·09	1·26	34·57	1·52	61·59	1·78	84·50
1·01	1·57	1·27	35·71	1·53	62·53	1·79	85·70
1·02	3·03	1·28	36·87	1·54	63·43	1·80	86·90
1·03	4·49	1·29	38·03	1·55	64·26	1·81	88·30
1·04	5·96	1·30	39·19	1·56	65·08	1·82	90·05
1·05	7·37	1·31	40·35	1·57	65·90	1·83	92·10
1·06	8·77	1·32	41·50	1·58	66·71	1·831	92·30
1·07	10·19	1·33	42·66	1·59	67·59	1·832	92·52
1·08	11·60	1·34	43·74	1·60	68·51	1·833	92·75
1·09	12·99	1·35	44·82	1·61	69·43	1·834	93·05
1·10	14·35	1·36	45·88	1·62	70·32	1·835	93·43
1·11	15·71	1·37	46·94	1·63	71·16	1·836	93·80
1·12	17·01	1·38	48·00	1·64	71·99	1·837	94·20
1·13	18·31	1·39	49·06	1·65	72·82	1·838	94·60
1·14	19·61	1·40	50·11	1·66	73·64	1·839	95·00
1·15	20·91	1·41	51·15	1·67	74·51	1·840	95·60
1·16	22·19	1·42	52·15	1·68	75·42	1·8405	95·95
1·17	23·47	1·43	53·11	1·69	76·30	1·8410	97·00
1·18	24·76	1·44	54·07	1·70	77·17	1·8415	97·70
1·19	26·04	1·45	55·03	1·71	78·04	1·8410	98·20
1·20	27·32	1·46	55·97	1·72	78·92	1·8405	98·70
1·21	28·58	1·47	56·90	1·73	79·80	1·8400	99·20
1·22	29·84	1·48	57·83	1·74	80·68	1·8395	99·45
1·23	31·11	1·49	58·74	1·75	81·56	1·8390	99·70
1·24	32·28	1·50	59·70	1·76	82·44	1·8385	99·95
1·25	33·43	1·51	60·65	1·77	83·32		

TABLE IX.

STRENGTHS AND SP. GR. OF OLEUMS (*Molinari's Chemistry*).

Sp. gr. at 35° C.	100 parts by weight correspond to			Sp. gr. at 35° C.	100 parts by weight correspond to		
	SO_3		H_2SO_4 (monohydrate)		SO_3		H_2SO_4 (monohydrate)
	Total	Free			Total	Free	
1·8186	81·63	0	100·00	1·9749	91·18	52	111·70
1·8270	81·99	2	100·45	1·9760	91·55	54	112·15
1·8360	82·36	4	100·90	1·9772	91·91	56	112·60
1·8425	82·73	6	101·35	1·9754	92·28	58	113·05
1·8498	83·09	8	101·80	1·9738	92·65	60	113·50
1·8565	83·46	10	102·25	1·9709	93·02	62	113·95
1·8627	83·82	12	102·70	1·9672	93·38	64	114·40
1·8692	84·20	14	103·45	1·9636	93·75	66	114·85
1·8756	84·56	16	103·60	1·9600	94·11	68	115·30
1·8830	84·92	18	104·05	1·9564	94·48	70	115·75
1·8919	85·30	20	104·50	1·9502	94·85	72	116·20
1·9020	85·66	22	104·95	1·9442	95·21	74	116·65
1·9092	86·03	24	105·40	1·9379	95·58	76	117·10
1·9158	86·40	26	105·85	1·9315	95·95	78	117·55
1·9220	86·76	28	106·30	1·9251	96·32	80	118·00
1·9280	87·14	30	106·75	1·9183	96·69	82	118·45
1·9338	87·50	32	107·20	1·9115	97·05	84	118·90
1·9405	87·87	34	107·65	1·9046	97·42	86	119·35
1·9474	88·24	36	108·10	1·8980	97·78	88	119·80
1·9534	88·60	38	108·55	1·8888	98·16	90	120·25
1·9584	88·97	40	109·00	1·8800	98·53	92	120·70
1·9612	89·33	42	109·45	1·8712	98·90	94	121·15
1·9643	89·70	44	109·90	1·8605	99·26	96	121·60
1·9672	90·08	46	110·35	1·8488	99·63	98	122·05
1·9702	90·44	48	110·80	1·8370	100·00	100	122·50
1·9733	90·81	50	111·25				

TABLE X.

SP. GR. $\left(\frac{15^\circ}{4^\circ}\right)$ AND STRENGTHS OF SODIUM HYDROXIDE SOLUTIONS.

Parts by weight of NaOH *in* 100 *parts by weight of solution.*

Sp. gr.	NaOH	Sp. gr.	NaOH	Sp. gr.	NaOH	Sp. gr.	NaOH
1·012	1	1·192	17	1·351	32	1·508	47
1·023	2	1·202	18	1·363	33	1·519	48
1·035	3	1·213	19	1·374	34	1·529	49
1·046	4	1·225	20	1·384	35	1·540	50
1·059	5	1·236	21	1·395	36	1·550	51
1·070	6	1·247	22	1·405	37	1·560	52
1·081	7	1·258	23	1·415	38	1·570	53
1·092	8	1·269	24	1·426	39	1·580	54
1·103	9	1·279	25	1·437	40	1·591	55
1·115	10	1·290	26	1·447	41	1·601	56
1·126	11	1·300	27	1·456	42	1·611	57
1·137	12	1·310	28	1·468	43	1·622	58
1·148	13	1·321	29	1·478	44	1·633	59
1·159	14	1·332	30	1·488	45	1·643	60
1·170	15	1·343	31	1·499	46	1·748	70
1·181	16						

TABLE XI.

Sp. gr. $\left(\frac{15^\circ}{4^\circ}\right)$ and Strengths of Ammonium Hydroxide Solutions (Lunge).

Parts by weight of NH_3 *in* 100 *parts by weight of solution.*

Sp. gr.	NH_3	Sp. gr.	NH_3	Sp. gr.	NH_3	Sp. gr.	NH_3
1·000	0·00	0·970	7·31	0·940	15·63	0·910	24·99
0·998	0·45	0·968	7·82	0·938	16·22	0·908	25·65
0·996	0·91	0·966	8·33	0·936	16·82	0·906	26·31
0·994	1·37	0·964	8·84	0·934	17·42	0·904	26·98
0·992	1·84	0·962	9·35	0·932	18·03	0·902	27·65
0·990	2·31	0·960	9·91	0·930	18·64	0·900	28·33
0·988	2·80	0·958	10·47	0·928	19·25	0·898	29·01
0·986	3·30	0·956	11·03	0·926	19·87	0·896	29·69
0·984	3·80	0·954	11·60	0·924	20·49	0·894	30·37
0·982	4·30	0·952	12·17	0·922	21·12	0·892	31·05
0·980	4·80	0·950	12·74	0·920	21·75	0·890	31·75
0·978	5·30	0·948	13·31	0·918	22·39	0·888	32·50
0·976	5·80	0·946	13·88	0·916	23·03	0·886	33·25
0·974	6·30	0·944	14·46	0·914	23·68	0·884	34·10
0·972	6·80	0·942	15·04	0·912	24·33	0·882	34·95

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